Carbon Deposition on Nickel-based Catalyst during Bio-syngas Methanation in a Fluidized Bed Reactor

Feng Fei1, a, Cao Hui2, Zhang Lei1, Jin Liang4

1 School of intelligent manufacturing, Nanjing Polytechnic Institute, Nanjing 210048, China
2 Planning and Land Resource Bureau, Nanjing Jiangbei New area Management Committee, Nanjing 210032, China
3 corresponding author: fnfa1997@163.com.

Abstract. Carbon deposition on the nickel-based catalyst is a common phenomenon during the bio-syngas methanation process. A nickel-based catalyst supported on γ-Al2O3 was prepared with impregnation method. Carbon deposition tests were carried out in a fluidized bed reactor to explore the carbon deposition phenomenon and the spent catalysts were collected for TG and gas sorption analysis. The TG analysis showed that the weight of the deposited carbon occupied about 1.90wt% of the total spent catalyst. The nitrogen sorption analysis presented that the BET surface area of the spent catalyst was much less than that of the raw catalyst and pore volume and width were also less than those of the raw catalyst. This is because during the methanation process, some kinds of stable carbon are formed besides active carbon and they accumulate on the catalyst surface, which can cause the encapsulation of the active site and block the tiny porous channels on the catalyst surface. All of these may explain the textural properties changes between raw catalyst and spent catalyst. These findings also help to furtherly improve and design the highly carbon-resistant catalysts.

1. Introduction
Carbon deposition is a common phenomenon in the bio-syngas methanation for nickel-based catalysts, which often causes the loss of catalyst reactivity. Researchers in the whole world have done a lot of work to investigate and get rid of this phenomenon during the synthetic natural gas (SNG) production from coal or biomass [1,2]. These researches cover catalyst supports, methanation reactor designs and preparation methods, etc. For instance, Bai etc. [3] found that the operating conditions had great effects on the carbon deposition and low operating pressure and space velocity were in favour of the production of carbon deposits. Liu etc. [4] prepared the Ni/Al2O3 catalysts modified by ZrO2 and the experimental results showed that this kind of catalysts through modification were more stable and had high capability of anti-carbon deposition.

However, there is still no consistent opinion on the carbon deposition mechanism of nickel-based catalysts although researchers have made great efforts to investigate this phenomenon. Most of the analysis were focused on the sole catalyst particle or some part of one particle. As a result, it is necessary to analyse the catalyst surface changes during the carbon deposition from the respect of the total particles.

Al2O3 is a kind of support most commonly used for nickel-based catalyst because of its high surface area and thermal stability [5]. We therefore used γ-Al2O3 in our study as the catalyst support. As for the reactor, two types of methanation reactor are often used in the methanation process: fix bed
reactors and fluidized bed reactors. Fluidized bed reactors have the advantage of high heat and mass transfer and they can quickly remove the reaction heat produced during the methanation process, which is crucial for the methanation reactions [6]. Consequently, we used this kind of reactor to carry out our carbon deposition tests so that our research work can provide guidelines to the reactor design.

In short, in this paper, we tried to investigate the carbon deposition on the nickel-based catalyst in a pressurized fluidized bed reactor and analyse the evolution of the catalyst surface. In this way, we hoped we could provide some productive points to the industry for improving the carbon-resistance of the nickel-based catalysts.

2. Experimental

2.1 Preparation of catalyst sample

The raw catalyst (16 wt% of NiO) for this study is a kind of nickel-based catalyst supported on γ-Al₂O₃. This catalyst was prepared with impregnation method and the pellet size was 60-100 mesh. For each run, the loading of fresh catalyst was 87g and the catalyst samples were tested in a fluidized bed reactor for 6h long.

2.2 Brief introduction of the testing equipment

The testing system was mainly composed by a fluidized bed reactor as shown in Figure 1, which was described in our previous work [7]. The operating condition for every run was 0.3MPa of the reaction pressure, 450°C of the reaction temperature and 10000h⁻¹ of the gas hourly space velocity (GHSV). The bio-syngas was simulated with high purity H₂ (99.99%) and CO (99.99%) with the H₂/CO molar ratio of 3. The whole system was heated by the furnace and N₂ (99.99%) was fed in as the internal standard gas at the beginning of each test. When the desired operating condition was achieved, the reaction gas (mixture of H₂ and CO) was input into the reactor and the reaction lasted for 6 hours. In the end of each test, the reaction gas was removed from the system while the standard gas (N₂) was still fed in until the system was cooled down. For every operating condition, the tests were carried out twice.

![Figure 1. Fluidized bed methanation system](image)

2.3 Catalyst characterization

The raw catalysts and spent ones were analyzed with a thermal gravimetric analyzer (TGA) and an ASAP 2020M automated gas sorption analyzer. Two gases were used in the TG analysis. At low temperature (<100°C), nitrogen was fed into the analyzer to remove the moisture on the catalyst at the first stage. Air was supplied as the oxidizer to react with the carbon deposited on the catalyst surface when first stage (moisture removal) was over. In this way, we tried to figure out the weight change after the carbon deposition on the catalyst surface with TGA and then calculate the weight loss percentage with the time and temperature.
For the surface topography change of the raw and spent catalysts, the N$_2$ adsorption-desorption measurements were applied with high purity nitrogen as adsorbing medium at 77K in the ASAP 2020M automated gas sorption analyzer. The specific surface area was then calculated with Brunauer-Emmett-Teller (BET) method. The pore volume and pore size distribution of the catalysts was both determined with Barret-Joyner-Hallender (BJH) method.

These measurements were carried out on both the raw catalyst and the spent ones for comparison.

3. Results and discussions

3.1 Weight changes due to carbon deposition

The weight change with time of the spent catalyst was shown in Figure 2 and the weight loss with the temperature was shown in Figure 3, which presented the results from the thermal gravimetric analyzer.

As shown in Figure 2 and 3, at the beginning of the TG analysis, the nitrogen was directed into the analyzer for the first 40mins and the temperature increased to 100°C with the time. Obviously, there was no weight loss for the first 9mins because the furnace temperature was below the water vaporizing point and there was little water vaporizing from the spent catalysts. With the temperature increasing, water on the spent catalyst surface began to emit to the flow gas. This process lasted about 30mins and almost all the water was removed from the catalyst. The moisture weight percentage on the spent catalyst was 1.40wt%. Then, the air was fed into the analyzer and the reaction temperature was raised to 550°C. This process lasted 260mins until there was no weight change of the spent catalyst in the end of the analysis. There was an evident weight loss in the first 30mins of this stage and then the weight
decreased slowly and maintained almost stable eventually. In the exit of the analyzer, carbon dioxides were detected. This meant during the bio-syngas methanation process, there was carbon formed on the catalyst surface. This kind of carbon deposited on the catalyst surface could be converted to carbon dioxides and removed. The weight percentage of the deposited carbon was 1.90wt%, which meant carbon deposition was very serious in our study.

3.2 Textural properties of raw and spent catalysts
The textural properties of raw and spent catalysts were measured separately with the ASAP 2020M automated gas sorption analyser and the results were shown in Table 1. There are evident changes in the topography between raw and spent catalysts. After methanation, the surface area, pore volume and pore width of the spent catalysts are all less than those of the raw catalysts, especially for the surface areas. This is because the produced carbon deposits on the catalyst surface and blocks the pores on the surface, which therefore causes the surface area, pore volume and pore width to decrease after methanation reaction.

Table 1. Textural properties of raw and spent catalysts

| Samples                  | Raw catalysts | Spent catalysts |
|--------------------------|---------------|-----------------|
| BET surface areaa (m²/g) | 129           | 98              |
| BJH cumulative pore volumeb (cm³/g) | 0.24           | 0.20            |
| BJH average pore widthb (nm) | 15.3           | 14.4            |

Reaction condition: 0.3MPa, 10000h⁻¹, H₂/CO=3, 6h test, 450°C.

a Calculated by BET (Brunauer-Emmett-Teller) equation.
b BJH (Barret-Joyner-Hallender) desorption pore volume.

Figure 4. Pore size distributions of the spent catalysts
Reaction condition: 0.3MPa, 10000h⁻¹, H₂/CO=3, 6h test, 450°C
The gas sorption analyser also presents the pore size distribution on the surface of the spent catalyst. As shown in Figure 4, most of the pores on the catalyst surface are mesopores with their pore width of about 5nm to 50nm while there are few micro-pores or macro-pores. This pore width range becomes narrow when compared to our previous work.

3.3 Discussions
Carbon deposition is one of the major causes that lead to catalyst deactivation. From the perspective of chemical equilibrium, two reactions may cause the carbon deposition [8].

\[
2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}
\]  
(1)
Reaction (1) is a CO disproportionation reaction, which often takes place when the reaction temperature is lower than 500°C. Reaction (2) is the methane decomposition reaction, which often happens at the reaction temperature over 500°C. As a result, in our study, the main reaction that causes carbon deposition is CO disproportionation reaction and this is an extensive exothermic reaction and thus high reaction temperature is not favorable. Under this condition, researchers [3] even found that a kind of amorphous carbon layers was formed on the catalyst surface at 400°C, which may stick to the surface and cause the catalyst deactivation gradually.

With regard to the bio-syngas methanation mechanism, the methanation process often includes four elementary steps. That is H₂ and CO adsorptions, CO dissociation, hydrogenation of adsorbed C. CO dissociation is the most important step while this step also may lead to the carbon production, as shown in Figure 5 [9]. A kind of atomic carbon, Cₐ, is formed through CO dissociation, which can be removed by the carbon hydrogenation step. However, some other types of carbons (polymeric carbon Cₚ, vermicular filaments Cᵥ or bulk Ni carbide Cₐ) may also form when the methanation temperature is even under 500°C. That is when the reaction temperature is over 325°C, the active carbon Cₐ may be converted to Cₚ or Cᵥ, which are more stable and exhibit some structures like surface film or vermicular carbon [10,11]. If these types of amorphous and filamentous carbons accumulate on the catalyst surface due to carbon deposition, the active centers gradually become encapsulated by these inactive carbons.

\[
\text{C} \rightarrow \text{C}_\text{β} \rightarrow \text{C}_\text{α} \rightarrow \text{C}_\text{γ}
\]

Figure 5. Conversion of carbon monoxide to different forms of carbon [9]

In addition to encapsulation, the deposited carbon can plug the catalyst micro and meso pores and even destroy the catalyst pellets [12,13]. This is in line with the analysis results in Table 1 and Figure 4. That is the textural properties of the spent catalysts all decrease compared to the raw catalysts, which would lead to the decline of the catalytic performance as the methanation process goes on.

4. Conclusions
In this paper, we collected the spent nickel-based catalyst samples in the fluidized bed methanation reactor and analysed them with TGA and automated gas sorption analyzer so that to describe and analyze the carbon deposition phenomenon on the nickel-based catalyst from the perspective of whole particles.

The TGA results showed that 1.90 wt% of the total spent catalyst was the deposited carbon, which meant serious carbon deposition occurred during the bio-syngas methanation on the nickel-based catalyst. The gas sorption analysis furtherly indicated that the carbon deposition caused dramatic changes in the catalyst textural properties. The surface area, pore volume and pore width of the spent catalyst were all less than those of the raw catalyst.

Under the methanation condition in this paper, some kinds of stable carbons produced besides the active carbon in the methanation process. These deposited carbons resulted in the catalyst deactivation and declined the catalytic performance.

In conclusion, it is necessary to find a way to improve the anti-coke capability of the nickel-based catalysts in the future.
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