

UTILIZATION PROPERTIES OF Ni-Pd/Al₂O₃ CATALYST SUPPORTED ON ALUMINA BASED FOAM

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Abstract

The aim of this study was to examine utilization properties of Ni-Pd/Al₂O₃ catalyst supported on α-Al₂O₃ based foam in the dry methane reforming. The catalyst was synthesized by using aerosol route. Non-calcined chloride precursors for Ni and Pd were reduced by hydrogen at very low temperature of 533 K. The reforming test was carried out for 3 h. Standing time was set to 1 h for each of the following temperatures: 873, 973 and 1023 K. Yields of CO and H₂ were determined and conclusions on selectivity, catalytic activity and stability were made on the basis of obtained results.

Keywords: Nickel-based catalyst, Alumina based foam, Dry methane reforming

Introduction

In the recent research, dry reforming of methane (DRM) have drawn considerable attention due to processing of two main greenhouse gases, CO₂ and CH₄. The DRM process is carried out over noble and non-noble metal based catalysts at temperatures from 973 to 1173 K in order to produce synthesis gas. Synthesis gas is a mixture of CO and H₂ and it is a valuable raw material used, as an example, for liquid fuels production. Considering high reactivity and favorable price of Ni, Ni-based catalysts such as Ni/Al₂O₃ are suitable for utilization in industrial conditions [1, 2]. Main disadvantages of Ni-based catalysts are rapid deactivation, caused by deposition of byproducts on active particles and sintering of active particles at high temperatures. To overcome these problems, Ni-based catalysts can be modified by only 0.4 to 0.5 wt. % of Pd [3,4].

Ceramic foams as catalyst supports have low pressure drops during the fluid flow, good mass transfer and good heat conductivity [5]. Therefore, the authors previously prepared Ni-Pd/Al₂O₃ catalyst supported on α-Al₂O₃ based foam via aerosol route [6]. The foam was synthesized as described earlier [7]. Using of chloride precursors for Ni and Pd provided elimination of the calcination and the

catalyst was reduced at 533 K [6]. Moreover, oxides obtained by calcination have lower reducibility than chlorides [8].

The present study aims to examine utilization properties of Ni-Pd/Al₂O₃ catalyst in the DRM process. Yields of H₂ and CO at three process temperatures were determined and conclusions on selectivity, activity and stability of the catalyst were made.

Experimental

To prepare the catalyst, NiCl₂·6H₂O, PdCl₂ (MERCK, pro analysis) and α-Al₂O₃ based foam were used. The foam was synthesized earlier by polymer replication [7]. According to previously presented method [6], chloride solution was ultrasonically nebulized and deposited to the foam at 473 K. After drying at 473 K for 1 h, the sample was reduced with H₂ (flow rate: 20 L h⁻¹) at 533 K for 1.5 h. Metal content was 20 wt. % of Ni modified with 0.1 wt. of % Pd. After the reduction, microstructure of the catalyst was investigated by using a JEOL JSM-5800LV scanning electron microscope (SEM).

Apparatus for the DRM experiment is presented in Fig. 1.

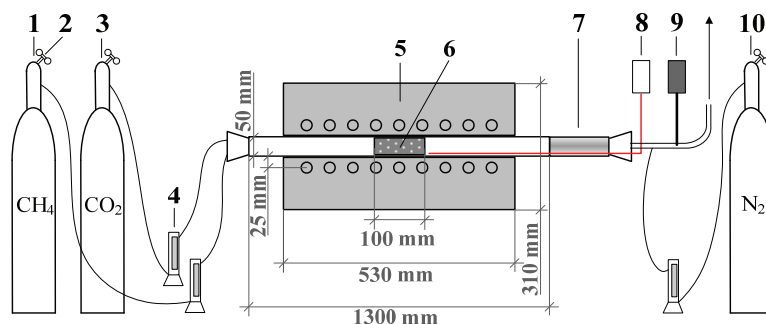


Fig. 1. Apparatus for the dry methane reforming: 1 – high-pressure CH₄ bottle, 2 – reducing valve, 3 - high-pressure CO₂ bottle, 4 - rotameter, 5 - electric resistance furnace, 6 – Ni-Pd/Al₂O₃ catalyst, 7 - water-cooled condenser, 8 - thermo couple, 9 – flue gas analyzer, 10 - high-pressure N₂ bottle

The reforming experiment was performed for 3 h in a quartz reactor at atmospheric pressure, without changing the catalyst. Standing time was 1 h at each of the following temperatures: 873, 973 and 1023 K. After reaching 873 K, inlet stream of CH₄ and CO₂ (CH₄:CO₂ = 1:1) was set to a total flow rate of 6 L h⁻¹ (24 L g⁻¹ h⁻¹). Flowing N₂ (2.5 L h⁻¹) was used to dilute outlet stream. CO and H₂ concentrations were measured with Testo 340 Flue Gas Analyzer. At the process temperature of 973 K, N₂ flow rate was set to 1.0 L h⁻¹ and remained constant until the end of the DRM experiment. To investigate stability of the catalyst, CO and H₂ concentrations were measured at 1023 K at the end of the DRM experiment. Yields of CO and H₂ were determined by using equations 1 and 2, taking into account the dilution with N₂. Based on CO and H₂ yields, the authors reached conclusions on activity, selectivity and stability of the catalyst.

$$Y_{CO} \% = \frac{C_{CO_{out}}}{C_{CH_4_{in}} + C_{CO_2_{in}}} \times 100 \quad (1)$$

$$Y_{H_2} \% = \frac{C_{H_2_{out}}}{2C_{CH_4_{in}}} \times 100 \quad (2)$$

Y_X represents yields of the products (vol. %), $C_{X_{in}}$ and $C_{X_{out}}$ denote concentration of gases in the inlet and outlet stream, respectively (mol).

Results and discussion

Morphology of surface of the reduced Ni-Pd/Al₂O₃ catalyst is presented in Fig. 2.

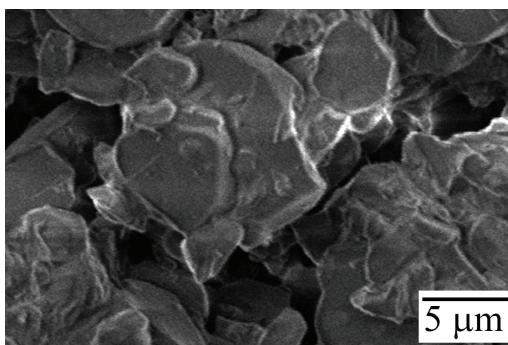


Fig. 2. Micrograph of Ni-Pd/Al₂O₃ reduced at 533 K for 1.5 h, metal content (wt. %): 20 % Ni and 0.1 % Pd

It was noted that, after the reduction at 533 K, relatively smooth metallic film was formed over the whole foam surface (Fig. 2). No undesirable agglomerates were detected and obtained surface morphology could be suitable for catalytic processes. Reduction of chloride precursors for Ni and Pd in flowing H₂ resulted in almost complete transfer to metallic phases. The chlorides reached a reduction degree of 98.2 wt. % [6]. Different than that, our previous study showed that only 20.0 wt. % of oxide precursors for Ni and Pd, obtained by calcination, was reduced at the same reduction conditions. Therefore, the synthesis of active catalytic components from chloride instead of oxide precursors can provide energy savings due to elimination of the calcination step [6]. In addition, after kinetic analysis of NiO and NiCl₂ reduction by H₂, the authors concluded that the chloride phase has higher reducibility [8].

Utilization properties of the prepared Ni-Pd/Al₂O₃ catalyst were examined in the DRM process. Results obtained at 873 K are presented in Fig. 3.

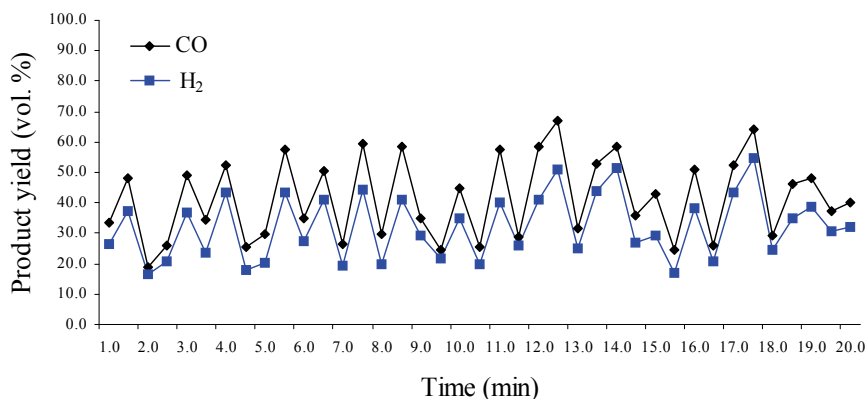


Fig. 3. CO and H₂ yields at 873 K

The results obtained at 873 K varied in a great extent. CO yield ranged from 18.8 and 67.1 %, with mean value of 41.5 %. Values of H₂ yield ranged from 16.6 and 54.8 %, and the mean value was 32.2 %. Nevertheless, nearly constant H₂/CO molar ratios were achieved during the period of 20 minutes, with the mean value of 0.8. Yields of CO and H₂ during the reforming at 573 K indicated the requirement for higher process temperature.

Results obtained at process temperature of 973 K are presented in Fig. 4.

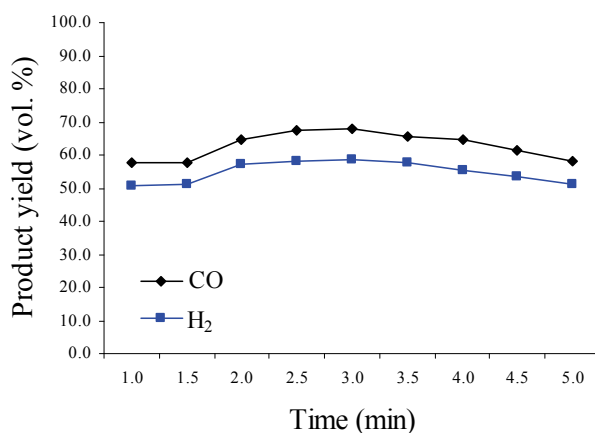


Fig. 4. CO and H₂ yields at 973 K

The reforming results significantly improved at the process temperature of 973 K. Obtained values varied in the following ranges: CO yield – from 57.7 to 68.0 % (mean value: 62.8 %) and H₂ yield – from 50.6 to 58.8 % (mean value: 54.8 %). Those yields were relatively constant. After 1.5 minutes, concentrations of CO and H₂ increased and then slightly declined after 3 minutes. Nearly constant and more favorable molar ratio of H₂ and CO was achieved than at 873 K, with the mean value of 0.9.

The reforming results at process temperature of 1023 K are shown in Fig. 5.

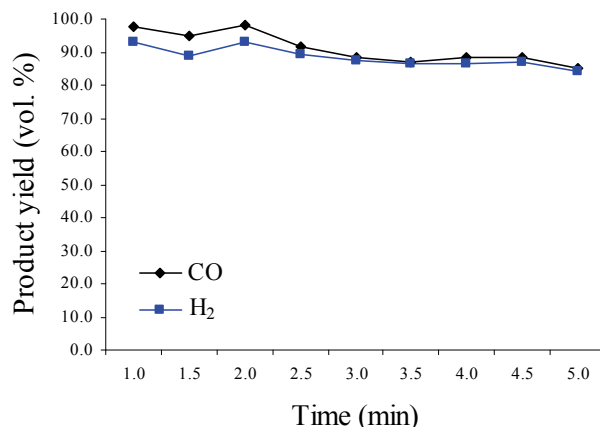


Fig. 5. CO and H₂ yields at 1023 K

Performance of the tested catalyst was the most pronounced at 1023 K, where yields of the main products reached nearly maximal values. CO yielded from 85.0 to 98.1 %, with the mean value of 91.0 %. H₂ yielded between 84.3 and 93.2 %, and the mean value was 88.5 %. A slight decrease of CO and H₂ yields was noted after 2 minutes. After 2.5 minutes, the yields reached close values and remained relatively constant until the end of the investigation. H₂/CO molar ratio had the most favorable mean value of 1.0 and was almost constant during the measuring. It was concluded that the catalyst had good selectivity for CO and H₂. High yields of those gases after 3 h of testing indicate that the catalyst possesses high activity and stability.

Conclusions

Performance of Ni-Pd/Al₂O₃ catalyst supported on α -Al₂O₃ based foam was examined in the dry methane reforming process. The catalyst was synthesized via aerosol route. To obtain Ni and Pd, corresponding chlorides were reduced with H₂ at 533 K, without previous calcination. Relatively smooth metallic film was formed over the foam surface. The reforming experiment lasted for 3 h at different temperatures, without changing the catalyst. Mean results of the reforming at 873 K were the following: CO yield – 41.5 %, H₂ yield – 32.2 % and H₂/CO molar ratio – 0.8. Considerable improvement of the reforming efficiency was achieved at 973 K. Mean values of CO and H₂ yields were 62.8 and 54.8 %, respectively. Mean H₂/CO molar ratio reached 0.9. The most favorable results were achieved at 1023 K, when mean yields of CO and H₂ reached 91.0 % and 88.5 %, respectively. Mean H₂/CO molar ratio was near 1.0. The catalyst was highly active and stable, and had good selectivity for CO and H₂.

Acknowledgements

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