

EXPLOITATION PROPERTIES OF Ni-Pd/Al₂O₃ CATALYST SUPPORTED ON CERAMIC FOAM

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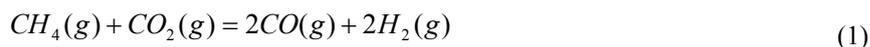
Abstract

The goal of this research was to examine exploitation properties of Ni-Pd/Al₂O₃ catalyst supported on α -Al₂O₃ based foam in the dry methane reforming. The catalyst was prepared by using aerosol method. Chloride precursors for Ni and Pd were reduced by hydrogen at low temperature of 533 K, without previous calcination. The reforming experiment was performed for 3 h, with standing time of 1 h for each of the following temperatures: 873, 973 and 1023 K. Conclusions on selectivity, catalytic activity and stability were made on the basis of CO and H₂ yields.

Keywords: Nickel, Palladium, Catalyst, Alumina based foam, Dry methane reforming

Introduction

Dry reforming of methane (DRM) is a significant technology in the field of sustainable development due to simultaneous processing of CO₂ and CH₄, as the main greenhouse gases. In the DRM process, noble or non-noble metal based catalysts and temperatures from 973 to 1173 K are required in order to produce synthesis gas. Synthesis gas (CO + H₂) is an important product which is used for liquid fuels production [1, 2]. The DRM process occurs according to the following chemical reaction [3]:



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Ni-based catalysts, mainly Ni/Al₂O₃, are suitable for utilization in industry because of high reactivity and favorable price of Ni [1, 2]. Ni-based catalysts are prone to rapid deactivation, caused by deposition of by-products on active surfaces and sintering of active metallic particles at high temperatures. In order to avoid deactivation, these catalysts can be modified by only 0.4 to 0.5 wt. % of Pd [4, 5].

Catalyst supports such as reticulated ceramic foams exhibit low pressure drops during the fluid flow, good mass transfer and good heat conductivity [6]. In the earlier work, the authors prepared Ni-Pd/Al₂O₃ catalyst supported on α -Al₂O₃ based foam by using aerosol method [7]. The foam was obtained as previously described [8]. Using of chloride precursors for Ni and Pd resulted in elimination of calcination step and very low reduction temperature – 533 K [7]. Furthermore, oxides formed by calcination have lower reducibility than chlorides [9].

The aim of this research is to examine exploitation properties of Ni-Pd/Al₂O₃ catalyst in the DRM process. Yields of H₂ and CO enabled to reach conclusions on selectivity, activity and stability of the catalyst.

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 [8]. According to previously presented method [7], 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).

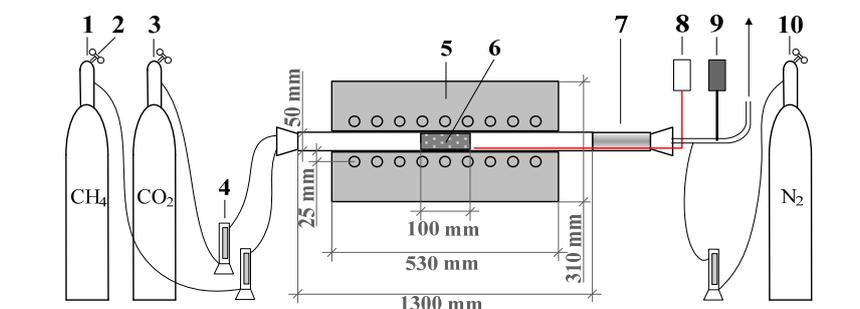
Apparatus and technological scheme for the DRM experiment are presented in Fig. 1 (a) and (b).

The DRM experiment was performed in a quartz reactor at temperatures of 873, 973 and 1023 K, without changing the catalyst. After reaching 873 K, inlet stream of CH₄ and CO₂ was introduced into the reactor. Process temperatures were changed during the experiment. CO and H₂ concentrations were measured with Testo 340 Flue Gas Analyzer while flowing N₂ was used to dilute outlet stream. In order to investigate stability of the catalyst, CO and H₂ concentrations were measured at 1023 K at the end of the experiment. Yields of CO and H₂ were determined by using equations (2) and (3), considering the dilution with N₂. Calculation was carried out by taking into account theoretical values of the yields for complete inlet gas reforming, equation (1). Based on CO and H₂ yields, the authors reached conclusions on activity, selectivity and stability of the catalyst.

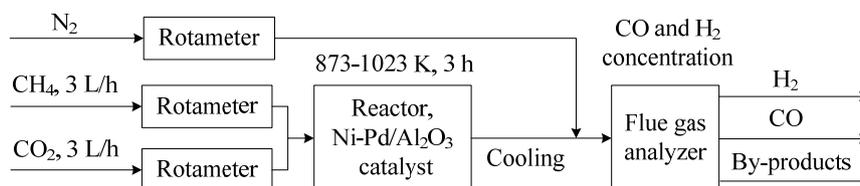
The DRM experiment parameters were the following:

- total process time: 3 h,
- process temperatures: 873, 973 and 1023 K,
- standing time at each temperature: 1 h,
- atmospheric pressure,
- inlet stream molar ratio: CH₄/CO₂ = 1,
- total flow rate of inlet stream: 6 L h⁻¹ (24 L g⁻¹ h⁻¹),
- N₂ flow rate at 873 K: 2.5 L h⁻¹,

- N₂ flow rate at 973 and 1023 K: 1.0 L h⁻¹ (constant until the end of the experiment).



(a)



(b)

Fig. 1. (a) 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
(b) Technological scheme of the dry methane reforming

$$Y_{CO} \% = \frac{C_{CO_{out}}}{C_{CH_4_{in}} + C_{CO_2_{in}}} \times 100 \quad (2)$$

$$Y_{H_2} \% = \frac{C_{H_2_{out}}}{2C_{CH_4_{in}}} \times 100 \quad (3)$$

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

Results and discussion

Surface morphology of the reduced Ni-Pd/Al₂O₃ catalyst is presented in Fig. 2.

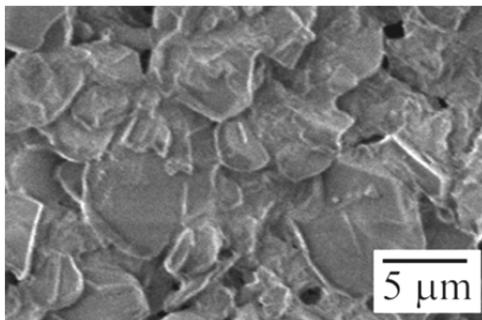


Fig. 2. Micrograph of Ni-Pd/Al₂O₃ reduced at 533 K for 1.5 h, metal content (wt. %): 20 % Ni and 0.1 % Pd

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 resulted in almost complete transfer to metallic phases. The chlorides reached a reduction degree of 98.2 wt. % [7]. 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 catalytic components from chloride instead of oxide precursors can provide energy savings due to elimination of the calcination step [7]. In addition, after kinetic analysis of NiO and NiCl₂ reduction by H₂, the authors concluded that the chloride phase has higher reducibility [9].

Results of the DRM process are presented in Fig. 3.

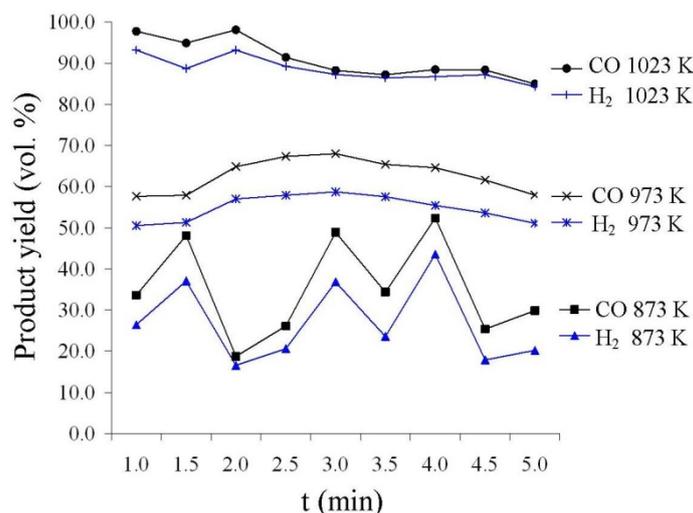


Fig. 3. CO and H₂ yields at: 873 K, 973 K and 1023 K

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 873 K indicated the requirement for higher process temperature. 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. 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

Selectivity, activity and stability of Ni-Pd/Al₂O₃ catalyst supported on α -Al₂O₃ based foam were examined in the dry methane reforming experiment. The catalyst was previously prepared by using aerosol method. Ni and Pd were synthesized from non-calcined chloride precursors by direct hydrogen reduction at 533 K. Metallic coating, obtained over the foam surface, was relatively smooth. The reforming process lasted for 3 h, without changing the catalyst. Mean results at process temperature of 873 K were the following: CO yield – 41.5 %, H₂ yield – 32.2 % and H₂/CO molar ratio – 0.8. Significant improvement of the process efficiency was achieved at 973 K. Mean values of CO and H₂ yields reached 62.8 and 54.8 %, respectively, and mean H₂/CO molar ratio was 0.9. The highest catalytic performance was achieved at 1023 K – mean yields of CO and H₂ reached values of 91.0 % and 88.5 %, respectively. Mean H₂/CO molar ratio was near 1.0. On the basis of obtained results, it was concluded that the catalyst had high activity, stability and selectivity for CO and H₂.

Acknowledgements

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References

- [1] J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei, Y. Sun, *Catal. Today* 148 (2009) 221-231.
- [2] J. Gao, Z. Hou, H. Lou, X. Zheng, *Fuel Cells: Technologies for Fuel Processing*, Chapter 7: Dry (CO₂) Reforming, Amsterdam, Netherlands, 2011. <http://www.sciencedirect.com/science/article/pii/B9780444535634100070>

- [3] W. Wang, C. Su, Y. Wu, R. Ran, Z. Shao, J. Power Sources 195 (2010) 402-411.
- [4] S. Damyanova, B. Pawelec, K. Arishtirova, J. L.G. Fierro, Int. J. Hydrogen Energ. 36 (2011) 10635-10647.
- [5] S. Damyanova, B. Pawelec, K. Arishtirova, J. L.G. Fierro, C. Sener, T. Dogu, Appl. Catal. B – Environ. 92 (2009) 250-261.
- [6] M. V. Twigg, J. T. Richardson, Chem. Eng. Res. Des. 80 (2002) 183-189.
- [7] V. Nikolić, Ž. Kamberović, Z. Anđić, M. Korać, M. Sokić, V. Maksimović, Int. J. Min. Met. Mater. 21 (2014) 806-812.
- [8] V. Nikolić, Ž. Kamberović, Z. Anđić, M. Korać, M. Sokić, Materials and Technology 48 (2014) 45-50.
- [9] M. Sokić, Ž. Kamberović, V. Nikolić, B. Marković, M. Korać, Z. Anđić, M. Gavrilovski, Sci. World J. (2015) <http://dx.doi.org/10.1155/2015/601970>