

NI-PD/AL₂O₃ CATALYST SUPPORTED ON RETICULATED CERAMIC FOAM FOR DRY METHANE REFORMING

Vesna Nikolić^{1*}, Željko Kamberović², Marija Korać², Miroslav Sokić³, Zoran Anđić⁴, Aleksandar Tomović⁵

¹*Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

²*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

³*Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franš d'Eperea 86, 11000 Belgrade, Serbia*

⁴*Innovation Center of the Faculty of Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia*

⁵*Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11120 Belgrade, Serbia*

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Abstract

In the present study, Ni-Pd/Al₂O₃ catalyst supported on α -Al₂O₃ based foam was prepared and evaluated in the dry methane reforming process. Corresponding metal chlorides were deposited to the foam surface by impregnation of the foam with ultrasonically aerosolized salt solutions at 473 K and drying at that temperature. Calcination step was excluded and the catalyst was reduced at very low temperature – 533 K. The reforming experiment lasted for 3 h, with standing time of 1 h at the following temperatures: 873, 973 and 1023 K. Conclusions on selectivity, catalytic activity and stability were reached on the basis of CO and H₂ yields.

Keywords: Nickel, Palladium, Catalyst, Reticulated ceramic foam, Dry methane reforming

Introduction

Syngas, i.e. CO and H₂ mixture, is a valuable raw material that can be used in the Fischer–Tropsch synthesis to produce liquid fuels. Dry reforming of methane (DRM) presents a promising technology for syngas production, because two greenhouse gases (CH₄ and CO₂) are simultaneously utilized. The DRM is commonly carried out at

* Corresponding author: Vesna Nikolić: vnikolic@tmf.bg.ac.rs

temperature range from 973 K to 1173 K, in the presence of catalysts based on noble and non-noble metals. However, Ni-based catalysts, e. g. Ni/Al₂O₃, are preferred in the recent research because Ni is highly reactive and has low price [1, 2]. Ni-based catalysts are rapidly deactivated due to formation of deposits on active sites and sintering of active particles at elevated temperatures. Deactivation resistance and activity of those catalysts are substantially enhanced by modification with only 0.4 to 0.5 wt. % of Pd. Pd improves Ni dispersion and reducibility of the catalysts because of hydrogen spillover effect [3, 4].

Conventional catalyst synthesis routes, such as impregnation, co-precipitation, sol-gel etc. require high temperatures in certain process steps. Calcination is performed at 773 K for 6 h [5] or at 823 K for 2 h [6], 4 h [3, 7] or 6 h [7]. The catalysts are reduced at: 823 K for 4 h [5], 873 K for 1 h [3], 973 K for 3 h [7] or at 1073 K for 2 h [6]. Juan-Juan et al. [8] prepared Ni/Al₂O₃ catalysts by hydrogen reduction of nickel salt at 773 K and 973 K for 2 h and avoided the calcination. These catalysts had good performance in the DRM tests [8]. Novel routes for the synthesis of fine metallic or catalyst particles involve ultrasonic aerosolization [9-11]. As an example, fine Fe-Ni powder is produced by pyrolysis and reduction of aerosolized chlorides, without the calcination [12].

Catalysts can be supported on reticulated ceramic foams, which exhibit good mass transfer, good heat conductivity and low pressure drops during the fluid flow [13-15]. Previously, authors synthesized Ni-Pd/Al₂O₃ catalyst via aerosol route [16]. The catalyst was supported on α -Al₂O₃ based foam prepared in our earlier work [17]. Chloride precursors for metals were almost completely reduced by hydrogen at 533 K. Utilization of chlorides instead of oxides in the production of catalysts can provide energy savings due to elimination of the calcination [16]. In addition, chlorides have higher reducibility than oxides obtained by calcination [18].

In the present study, Ni-Pd/Al₂O₃ catalyst was prepared and evaluated in the DRM process. Yield of the main reaction products, H₂ and CO, was measured at three different process temperatures. Obtained results were used to reach conclusions about selectivity, activity and stability of the catalyst.

Experimental

The following materials were used to synthesize the catalyst: NiCl₂·6H₂O, PdCl₂ (MERCK, pro analysis) and α -Al₂O₃ based foam prepared by polymer replication, as presented earlier [17]. The foam was impregnated by ultrasonically aerosolized solution of the chlorides at 473 K and dried at 473 K for 1 h. Dried, non-calcined sample with dehydrated chloride precursors was reduced at 533 K for 1.5 h (H₂ flow rate: 20 L h⁻¹). The catalyst had 20 wt. % of Ni, modified by addition of 0.1 wt. % Pd. Catalyst synthesis details and apparatus for the impregnation were as presented previously [16]. The catalyst surface was examined with a JEOL JSM-5800LV scanning electron microscope (SEM).

Catalytic performance of activated (reduced) catalyst was tested in the DRM process. Set-up for the experiment is presented in Fig. 1.

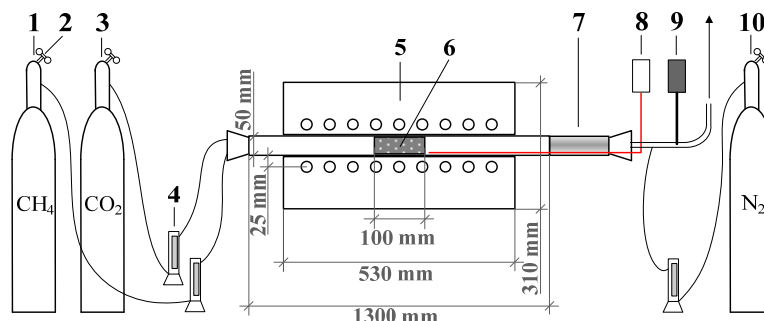


Fig. 1. Apparatus for the dry methane reforming: 1 – high-pressure CH₄ bottle, 2 – reducing valve, 3 – high-pressure CO₂ bottle, 4 – rotameter, 5 – electric resistance furnace, 6 – Ni-Pd/Al₂O₃ catalyst, 7 – water-cooled condenser, 8 – thermo couple, 9 – flue gas analyzer, 10 – high-pressure N₂ bottle

Total reforming time was 3 h, with standing time of 1 h at the following temperatures: 873, 973 and 1023 K. The reaction was carried out in a fixed-bed quartz reactor at atmospheric pressure. When temperature in the reactor reached 873 K, CH₄ and CO₂ (CH₄:CO₂ = 1:1) were allowed to pass through the catalyst bed at a total flow rate of 6 L h⁻¹ (24 L g⁻¹ h⁻¹). Outlet stream was diluted with N₂ (2.5 L h⁻¹). After reaching 973 K, N₂ flow rate was set to 1.0 L h⁻¹ and remained constant until the end of experiment. Concentrations of CO and H₂ in the outlet stream were measured by using Testo 340 Flue Gas Analyzer. The measurement at 1023 K was carried out at the end of the experiment. CO and H₂ yields were calculated according to equations 1 and 2, taking into account the dilution of the outlet stream.

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

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

Y_X stands for product yields (vol. %), $C_{X_{in}}$ and $C_{X_{out}}$ refer to molar concentration of gases in the inlet and outlet stream, respectively.

Conclusions on catalytic activity, selectivity for the main reaction products and stability were made on the basis of CO and H₂ yields obtained in the DRM process.

Results and discussion

SEM photograph of Ni-Pd/Al₂O₃ catalyst after the reduction of metal chlorides on the foam surface at 533 K for 1.5 h is presented in Fig. 2.

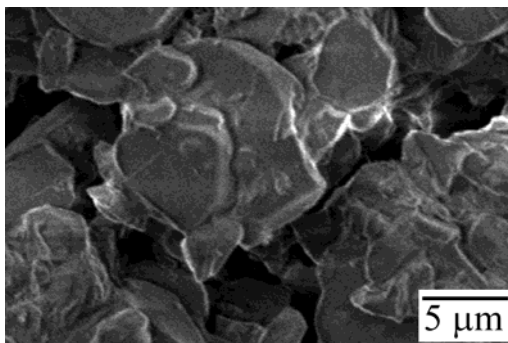


Fig. 2. Ni-Pd/Al₂O₃ reduced at 533 K, metal loading (wt. %): 20 % Ni and 0.1 % Pd

SEM analysis of the catalyst surface showed that relatively smooth metallic coating completely covered the foam (Fig. 2). Undesirable agglomerates, which can cause catalyst deactivation due to abrasion in a gas stream, were not detected. The chlorides of Ni and Pd were nearly completely reduced by hydrogen at 533 K for 1.5 h and reached a reduction degree of 98.2 wt. %. Utilization of chlorides instead of oxide precursors that are obtained by calcination can enable lower energy consumption because the calcination is avoided during the production of Ni-based catalysts [16]. Moreover, kinetic analysis of NiO and NiCl₂ hydrogen reduction confirmed that the oxide phase is more stable and less reducible than the chloride phase [18].

In the further course of investigation, synthesized catalyst was tested in the DRM process. Yields of CO and H₂ at reforming temperature of 873 K are presented in Fig. 3.

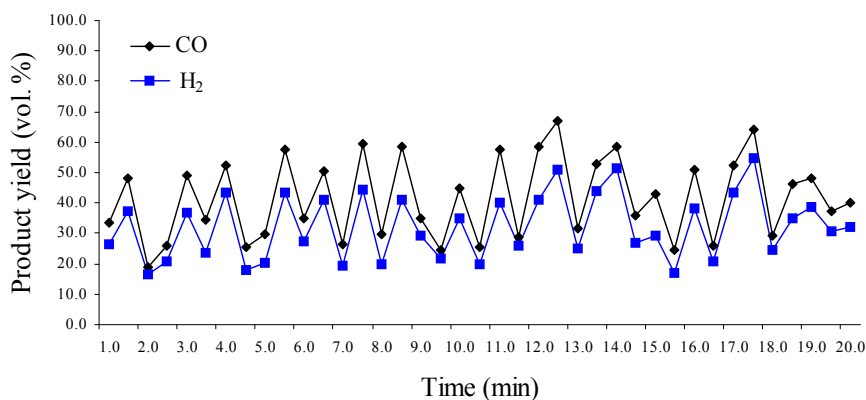


Fig. 3. Yields of CO and H₂ at 873 K

It was noted that differences between the results obtained at 873 K were considerable. Values of CO yield ranged between 18.8 and 67.1 %, and the average value was 41.5 %. H₂ yield varied between 16.6 and 54.8 % with an average value of 32.2 %. However, H₂/CO molar ratio was almost constant during 20 min. and reached an average value of 0.8. Obtained results indicated that higher process temperature was required.

The results of reforming at 973 K are shown in Fig. 4.

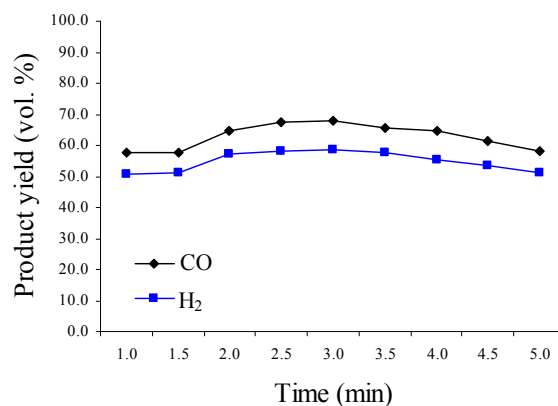


Fig. 4. Yields of CO and H₂ at 973 K

Higher process temperature (973 K) resulted in significant improvement of the reforming efficiency. Product yields varied in the following ranges: CO – from 57.7 to 68.0 % (62.8 % in average) and H₂ – from 50.6 to 58.8 % (average value of 54.8 %). CO and H₂ yields had relatively constant values during 5 min. An increase in concentrations of those gases was noticed after 1.5 min. and a slight decrease in their concentration occurred after 3 min. of measuring. Besides higher product yields, H₂/CO molar ratio was also more favorable than at 873 K. It was nearly constant during the measurement and reached an average value of 0.9. In order to further enhance the process efficiency and to examine stability of the catalyst, the process temperature was increased to 1023 K.

Product yields at the process temperature of 1023 K are presented in Fig. 5.

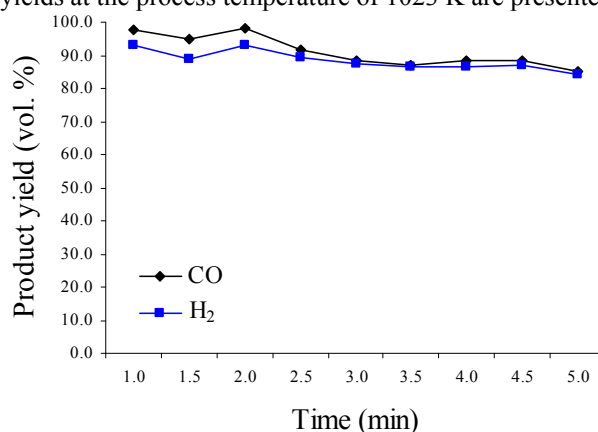


Fig. 5. Yields of CO and H₂ at 1023 K

The highest concentrations of CO and H₂ in the outlet stream were achieved by dry methane reforming at 1023 K. CO yield ranged from 85.0 to 98.1 %, with an

average value of 91.0 %. H₂ yielded between 84.3 and 93.2 %, 88.5 % in average. Obtained yields of CO and H₂ reached values close to maximum. After 2 min. of measuring, concentrations of both gases slightly declined. After 2.5 min, CO and H₂ concentrations started to have similar values and remained relatively constant until the end of the experiment. Moreover, H₂/CO molar ratio was almost constant and the most favorable. Its average value was near unity.

The Ni-Pd/Al₂O₃ catalyst, obtained by reduction of chloride precursors for Ni and Pd at 533 K, exhibited very good selectivity for the main reaction products at 1023 K. Considering that high CO and H₂ yields were maintained after 3 h of the DRM experiment, the conclusion is that the catalyst is highly active and stable.

Conclusions

The aim of this study was to evaluate utilization properties of Ni-Pd/Al₂O₃ catalyst supported on α -Al₂O₃ based foam and prepared by using aerosol route. Ni and Pd were obtained by hydrogen reduction of non-calcined metal chlorides at 533 K. Reduced catalyst contained 20 wt. % of Ni modified by 0.1 wt. % of Pd and had relatively smooth metallic coating without agglomerates over the foam surface. The dry methane reforming test was performed for 3 h at three temperatures, without changing the catalyst. The following average results were obtained at 873 K: CO yield – 41.5 %, H₂ yield – 32.2 % and H₂/CO molar ratio – 0.8. The results were significantly improved during the reforming at 973 K, when yields of CO and H₂ reached average values of 62.8 and 54.8 %, respectively. H₂/CO molar ratio was more favorable and it was averagely 0.9. Best catalytic performance was achieved at 1023 K. Average results were the following: CO yield – 91.0 %, H₂ yield – 88.5 % and H₂/CO molar ratio near 1.0. At that temperature, the catalyst exhibited high activity, good selectivity for CO and H₂ and high stability.

Acknowledgements

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