Nickel-based catalysts: Dependence of properties on nickel loading and modification with palladium

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Abstract
The aim of this study was comparative analysis of catalysts with 5 and 20 wt.% Ni loading, with and without Pd additive, and it included: determination of reduction degrees, investigation on microstructure by scanning electron microscopy and chemical analysis by energy-dispersive spectroscopy. Ni/Al2O3 and Ni-Pd/Al2O3 catalysts supported on α-Al2O3-based foams were synthesized by aerosol assisted impregnation. Impregnation of the foams by ultrasonically aerosolized chlorides was followed by drying at 473 K and hydrogen reduction at 533 and 633 K. Lower Ni loading resulted in higher reduction degrees. Ni loading of 20 wt.% enabled relatively uniform coverage of the foam with a metallic coating. Nearly complete reduction was achieved at both temperatures with activity modifier (Pd). Reduction degrees reached 99.4 and 98.2 wt.% at 533 K for 5 and 20 wt.% of Ni, respectively.

Key words: catalysts, Ni, Pd, modification, α-Al2O3-based foam, aerosol assisted impregnation.

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Metal-ceramic composite systems have been intensively researched in recent years because properties of a base material can be significantly enhanced by a small quantity of additive. For instance, there are composites such as metals reinforced with ceramic particles, dispersed in a metal matrix. Multiple strengthened Cu–Al2O3 systems, that could be suitable for using at elevated temperatures, are produced from ultra-fine and nanocomposite Cu–Al2O3 powders. Those powders can be synthesized by using novel method that includes spray drying of dissolved metal salts [1,2]. Composite catalytic materials with metallic particles dispersed on oxide supports are applied in various heterogeneous catalysis processes [3,4]. As an example, Ni/Al2O3 catalysts are commonly used for reforming of hydrocarbons [5–7]. Metallic particles are supported on γ-Al2O3 powder [5,8], reticulated α-Al2O3 foams [9,10], etc. Reticulated ceramic foams have high pore volumes and exhibit good mass transfer, good heat conductivity and low pressure drops for the duration of the fluid flow. Therefore, industrial application of ceramic foams as catalyst support could be favorable [10–12].

Although catalysts based on noble metals are common due to excellent catalytic activity, stability and selectivity [8], they are expensive for using in industry [13]. Ni is an effective alternative for noble metals because of low cost [6,7,14] and excellent catalytic properties [15]. Ni-based catalysts can be rapidly deactivated due to deposits that form on active sites and sintering of Ni at elevated temperatures. However, different supports, synthesis methods and catalytic activity modifiers (additives), improve catalytic activity, deactivation resistance and selectivity [6,7,14,15]. Modification with low amount of Pd (0.01 [16] to 0.3 wt. % [6]) greatly enhances catalysts properties. Catalyst’s activity and selectivity can be drastically deteriorated if metals are unevenly dispersed on support [6,16]. Conventional thermochemical methods for Ni-based catalysts synthesis include oxidative calcination and reduction by hydrogen (activation). Calcination causes formation of NiAl2O4 spinel phase, especially in the case of impregnation and γ-Al2O3 support. NiAl2O4 is hardly reducible and it can inhibit catalytic activity because of low amount of Ni particles [5–7]. As reported by Gayan et al. [17], α-Al2O3 support minimizes NiAl2O4 presence in the Ni/Al2O3 system obtained by impregnation. Novel methods that involve ultrasonically generated aerosols provide synthesis of fine spherical particles with precise stoichiometry and high purity [18–20]. Ultrasonic spray pyrolysis is favored in large scale production in industry [21]. Gurmen et al. [22] pyrolized and reduced ultrasonically aerosolized NiCl2 and FeCl3 solution in hydrogen flow. They obtained fine
spherical Fe–Ni particles in a single step, without calcination.

Previously, Ni/Al2O3 and Ni–M/Al2O3 catalysts, modified by additives M = Pd, Cu or Fe, were synthesized by aerosol assisted impregnation [23]. Oxides and chlorides were used as precursors for metals. Reduction of chloride precursor at 633 K, without previous calcination, resulted in optimal morphology of Ni coating. Modification with Pd enabled the highest reduction efficiency of all precursors [23] due to the hydrogen spillover effect [24, 25]. Chloride precursors for Ni–Pd coating reached significantly higher reduction degree (98.2 wt. %) than oxide precursors (20.0 wt. %) at 533 K [23].

On the basis of previously obtained results [23], Ni-based catalysts were synthesized by aerosol assisted impregnation using chlorides as precursors. Catalysts were supported on previously prepared α-Al2O3-based foams [26,27]. The aim of the presented research was to investigate dependence of catalysts properties from different Ni loading and from modification by Pd additive. Comparative analysis of the catalysts included determination of reduction degrees in hydrogen stream and microstructure development, which was investigated by scanning electron microscopy (SEM). An additional investigation included point analysis of reduced Ni–Pd/Al2O3 samples by energy-dispersive spectroscopy (EDS).

**EXPERIMENTAL**

Non-modified Ni/Al2O3 and modified Ni–Pd/Al2O3 catalysts with 5 and 20 wt.% Ni loading were synthesized by aerosol assisted impregnation method. Considering Ni–Pd/Al2O3 catalysts, Ni was modified with 0.1 wt.% of Pd. Used materials included: NiCl2⋅6H2O, PdCl2 (MERCK, pro analysis) and α-Al2O3-based foams. The foams were produced by polymer replication route that is described elsewhere [26,27]. First, the foams were pre-heated at 473 K in a tubular quartz reactor and then impregnated with aerosolized chloride solutions at that temperature. Subsequently, samples were dried at 473 K for 60 min in air. The catalysts were reduced by hydrogen at 533 and 633 K for 90 min. Set-up for the aerosol assisted impregnation and the synthesis method details are presented elsewhere [23].

Reduction degrees of chlorides on the foam surface were determined on the basis of chloride mass loss before and after hydrogen reduction. After the impregnation and subsequent drying at 473 K for 60 min, the samples were stored in desiccators with silica gel until the mass measurements to prevent absorption of moisture from the air. Mass ratio of chlorides and the foam was a known value. The reduction experiments were performed under static conditions as follows. First, the samples were set into a quartz tube and reaction area was purified by nitrogen flow. Then, nitrogen flow was stopped and hydrogen was introduced into the tube. Hydrogen flow was conducted through system for purification and drying that was consisted of: columns with silica gel, Cu powder and CaCl2 and wash bottle with H2SO4. A tubular electric resistance furnace was heated to the selected temperature and then the tube was put in. Measuring of reduction time started at that moment. Reduction of the dried samples was carried out at 533 and 633 K for 90 min (H2 flow rate 20 L/h). Reduced samples were placed in desiccators, cooled down to room temperature and their mass was determined afterward.

Microstructures of the samples after drying and after reduction experiments were investigated with a JEOL JSM-5800LV scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). SEM/EDS point analysis was carried out for Ni–Pd/Al2O3 catalysts with different metal loading, reduced at 533 K for 90 min.

**RESULTS AND DISCUSSION**

Reduction degrees of NiCl2 on the foam surface are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Temperature, K</th>
</tr>
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<tr>
<td>5 wt.% of Ni</td>
<td>60.2 67.7</td>
</tr>
<tr>
<td>20 wt.% of Ni</td>
<td>23.7 35.2</td>
</tr>
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</table>

As expected, higher reduction degrees were obtained at 633 than at 533 K for all the samples. However, when Ni loading was lower, significantly higher amount of NiCl2 was reduced at both temperatures due to the better exposure of NiCl2 particles to H2 flow when NiCl2 content was lower. These results could be explained with microstructures of the samples before and after hydrogen reduction (Figs. 1–3).

SEM photographs of the dried samples are presented in Fig. 1a and b. After SEM analysis of the dried sample with 5 wt.% Ni loading, presence of relatively unevenly distributed, fine, submicron-sized NiCl2 particles was noted, as shown in Fig. 1a. Agglomerates were not detected. Despite relatively uneven particle distribution, satisfying reduction degrees of NiCl2 were achieved at both temperatures (Table 1). These results could be explained by obtained morphology, because fine particles were non-agglomerated and, consequently, they had good exposure to H2. In addition, good mass and heat transfer through the foam was one of the reasons for...
satisfying reduction degrees. Figure 1b shows microstructure of the dried sample with 20 wt.% Ni loading. Higher NiCl₂ amount resulted in formation of cracked NiCl₂ crust, which completely covered the foam surface. This crust appeared to be thick on certain sites. A main reason for obtained cracks was dehydration of NiCl₂·6H₂O during the drying procedure, while filter-like behavior of the foam provided complete coverage with NiCl₂. Higher Ni loading resulted in lower reduction degrees at both temperatures (Table 1), due to absence of small individual NiCl₂ particles.

Figure 1. Sample dried at 473 K – NiCl₂/Al₂O₃, Ni loading: a) 5 and b) 20 wt.%.

Figure 2. Ni/Al₂O₃ reduced at 533 K, nominal Ni loading: a) 5 and b) 20 wt.%.

SEM photographs of the Ni/Al₂O₃ samples reduced at 533 K are presented in Fig. 2a and b. SEM photographs of the Ni/Al₂O₃ samples reduced at 633 K are presented in Fig. 3a and b.

After the reduction of Ni/Al₂O₃ with 5 wt.% Ni loading at both temperatures, small, island-like Ni particles were formed. Ni islands were isolated and submicron-sized particles were noted, as presented in Figs. 2a and 3a. No significant changes in the microstructures were noted after the reduction at each temperature. With 20 wt.% Ni loading, the samples reduced at both temperatures had similar microstructures: Ni coating relatively uniformly covered the foam surface, as presented in Figs. 2b and 3b. The reduction with H₂ led to disappearance of visible cracks. Formation of these microstructures could be explained by complex mass transport mechanism that occurred at elevated temperature during the reduction. At the reduction conditions, Ni particles gained sufficient mobility and migrated, which resulted in formation of contacts between particles and their growth. No agglomerates occurred in any of the reduced samples.

Reduction degrees of NiCl₂ with added PdCl₂, supported on the foam surface, are presented in Table 2.

Table 2. Reduction degrees, wt.%, of NiCl₂ with PdCl₂ on α-Al₂O₃ based foam after 90 min

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>533</td>
</tr>
<tr>
<td>5 wt.% Ni, 0.1 wt.% Pd</td>
<td>99.4</td>
</tr>
<tr>
<td>20 wt.% Ni, 0.1 wt.% Pd</td>
<td>98.2</td>
</tr>
</tbody>
</table>

Results of the reduction experiments showed minor differences in reduction degrees of the Ni–Pd/Al₂O₃ samples. All the samples were almost completely reduced at both investigated temperatures (Table 2). Although slightly higher reduction degrees were achieved at 633 K, obtained results indicate that lower reduction temperature can successfully be used for the catalysts synthesis, if the catalysts are modified with
Pd. The main reason for increased reduction efficiency was modification by Pd additive, which caused the hydrogen spillover effect. In general, this effect occurs in the presence of Pd surface, when H₂ molecules dissociate into atoms and rapidly diffuse into crystal lattices of Ni species [24,25].

SEM photographs of Ni–Pd/Al₂O₃ catalysts with 5 and 20 wt.% Ni loading, reduced at 533 K, are presented in Fig. 4a and b, respectively.

Similar microstructures were obtained for Ni–Pd/Al₂O₃ catalysts, reduced at 533 K, and for Ni/Al₂O₃ catalysts, reduced at 533 and 633 K. Ni–Pd/Al₂O₃ samples with 5 wt.% of Ni had fine, submicron-sized and isolated island-like particles dispersed on the foam surface, as presented in Fig. 4a. With higher Ni loading (20 wt.%), metallic coating relatively evenly covered the foam, as presented in Fig. 4b. Particles agglomeration did not occur in any of the samples. Modification with 0.1 wt.% of Pd enabled almost completed hydrogen reduction at 533 K. Ni-based catalysts prepared by conventional thermochemical methods are calcined before hydrogen reduction. The calcination treatment (e.g., at 823 K [6] or 873–923 K [5, 7]) provides forming of oxide mixtures that contain oxide precursors for catalytically active components. During that treatment, especially in the case of impregnation method, hardly reducible NiAl₂O₄ phase is commonly formed [5–7]. In addition, the authors concluded that Ni-based catalysts, prepared by using aerosol assisted impregnation and calcined at 773 K, had undesirable agglomerates on the α-Al₂O₃-based foam surface. Ni-based catalysts prepared by using the same method and obtained from chloride precursors reached significantly higher reduction degrees at same temperatures [23].

Point SEM/EDS analysis was performed for Ni–Pd/Al₂O₃ catalysts with different Ni loading, reduced at 533 K. Analyzed points are marked in Fig. 5a and b. The results are presented in Table 3.

<table>
<thead>
<tr>
<th>Metal loading</th>
<th>Mark</th>
<th>Ni</th>
<th>Al</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt.% Ni, 0.1 wt.% Pd</td>
<td>1</td>
<td>93.50</td>
<td>1.97</td>
<td>0.63</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.50</td>
<td>40.32</td>
<td>5.16</td>
<td>53.02</td>
</tr>
<tr>
<td>20 wt.% Ni, 0.1 wt.% Pd</td>
<td>1</td>
<td>94.21</td>
<td>1.53</td>
<td>0.58</td>
<td>3.68</td>
</tr>
</tbody>
</table>

Considering the sample with 5 wt.% Ni loading, island-like metallic particle mainly consisted of Ni. Pd was not detected due to very low concentration. Small amounts of Al, Si and O from the α-Al₂O₃ based foam were also detected. EDS analysis of point with no visible metallic particles showed predominance of elements that correspond to oxides in the α-Al₂O₃ based foam. With Ni loading of 20 wt.%, chemical analysis of a random point revealed that the main element in the metal coating was Ni. Similar to the sample with lower metal content, Pd was not detected because of low concentration. In addition, small amounts of Al, Si and O from the foam were noted. These results confirmed that higher metal loading enabled relatively uniform dispersion of metallic particles over the foam surface.

The conclusion is that Ni–Pd/Al₂O₃ catalysts supported on the α-Al₂O₃ based foams can successfully be produced by hydrogen reduction of chloride instead of oxide precursors, without the calcination step. Chloride precursors for Ni and Pd can be reduced at very low temperature (533 K). Optimal metal loading is 20 wt.%
of Ni modified by 0.1 wt.% Pd due to the relatively even coverage of the foam surface with metallic coating.

CONCLUSION

A comparative analysis of catalysts with 5 and 20 wt.% of Ni, with Pd and without additive, was conducted. The catalysts were supported on α-Al2O3-based foams and prepared by aerosol assisted impregnation. Before hydrogen reduction, samples with 5 wt.% of Ni had submicron-sized, non-agglomerated, isolated NiCl2 particles. Cracked NiCl2 crust enveloped the whole foam surface in the case of 20 wt.% of Ni. Higher reduction degrees were reached with lower Ni loading at 533 and 633 K. Reduced Ni/Al2O3 and Ni–Pd/Al2O3 samples had similar microstructures for the same Ni content. With 5 wt.% of Ni, isolated, island-like, submicron-sized particles were formed. Sample with 20 wt.% of Ni had metallic coating without agglomerates and visible cracks that relatively evenly covered the whole foam surface. Ni–Pd/Al2O3 catalysts were nearly completely reduced at both temperatures. Their reduction degrees reached 99.4 and 98.2 wt.% for 5 and 20 wt.% Ni loading, respectively, at 533 K. Optimal metal loading in the produced catalysts is 20 wt.% of Ni and the addition of 0.1 wt.% Pd because the foam surface is relatively uniformly covered with metallic coating. Obtained results indicate that Ni-based catalysts, modified with Pd, can successfully be synthesized without the calcination step and can be reduced at lower temperature.

Acknowledgements

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REFERENCES

IZVOD

Katalizatori na bazi nikla: zavisnost svojstava od sadržaja nikla i modifikacije paladijumom

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(Naučni rad)

Cilj predstavljenog istraživanja bila je uporedna analiza svojstava katalizatora na bazi nikla, sa sledećim sadržajem metala: 5 i 20 mas. % Ni, bez dodatka i sa dodatkom Pd. Ni/Al₂O₃ i Ni–Pd/Al₂O₃ katalizatori su sintetisani metodom impregnacije potpomognute ultrazvučnim raspršivanjem. Kao nosači katalitički aktivnih materija korišćene su keramičke pene na bazi α-Al₂O₃. Uporedna analiza svojstava sintetisanih katalizatora obuhvatala je: određivanje stepena redukcije uzoraka u struji vodonika, praćenje razvoja mikrostrukture metodom skenirajuće elektronske mikroskopije i ispitivanje hemijskog sastava u tački metodom energetsko disperznih spektroskopija. Radi sinteze katalizatora, nosači odnosno pene su pregreni u cevnim reaktorima na 473 K i impregnirane ultrazvučnim raspršenim rastvorima klorida metala. Nakon impregnacije, uzorci su sušeni na 473 K radi dehidratacije, a zatim redukovani u struji vodonika na 533 i 633 K. Kod uzoraka sa nižim sadržajem Ni, dobijeni su viši stepeni redukcije. Svi uzorci sa dodatkom Pd, kao modifikatorima aktivnosti, gotovo su u potpunosti bili redukovani na oba ispitivane temperature. Kod ovih uzoraka na van temperaturi od 533 K stepeni redukcije dostigli su 99,4 i 98,2 mas.% za sadržaj Ni od 5 i 20 mas.%, redom. Optimalni sastav proizvedenih katalizatora je 20 mas.% Ni i dodatak od 0,1 mas.% Pd, čime se postiže relativno ravnomerna prekrivenost cele površine pene slojem metala. Dobijeni rezultati ukazuju na to da se katalizatori na bazi Ni, modifikovani dodatkom Pd, uspešno mogu sintetisati bez koraka žarenja i redukovati na izuzetno niskoj temperaturi (533 K).