

## **SYNTHESIS OF CATALYTIC MATERIALS BASED ON SYSTEM Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Supported On Monolith Ceramic Foams**

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### **Abstract**

In the present investigation, nanostructured Ni/Al<sub>2</sub>O<sub>3</sub> catalyst supported on reticulated alumina-mullite foam was synthesized by aerosol assisted coating. The synthesis process was optimized from the technological and economic aspect. Ultrasonically generated NiCl<sub>2</sub> water solutions were applied to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite foam in a tubular quartz reactor. The first procedure involved calcination at 773 K for 1 h in order to obtain NiO/Al<sub>2</sub>O<sub>3</sub> precursor. The second procedure involved drying at 473 K for 1 h without oxidation. The activation step involved hydrogen reduction at 633 K. The effectiveness of the low-temperature hydrogen reduction was compared for those systems. It was determined that the samples were reduced in a high degree at 633 K for 90 minutes and the hydrogen flow rate of 20L/h. However, SEM of calcined sample shows presence of agglomerates. The samples reduced from NiCl<sub>2</sub> had no agglomerates and the metallic phase was homogeneously dispersed compared to the samples obtained by NiO reduction. The most probable reason for the effective low-temperature reduction was the formation of thin coatings consisted of oxide and chloride precursors for the catalytically active components. XRD analyse of the samples after the reduction at 633 K for 90 minutes showed only metallic nickel, alumina and mullite phases. Residual phases of NiO and NiCl<sub>2</sub>, as well as NiAl<sub>2</sub>O<sub>4</sub>, were not detected. The production process can be simplified and economically more favourable by avoiding the calcination step.

*Keywords: Nickel; Alumina; Reticulated foam; Catalyst; Aerosol assisted coating*

### **Introduction**

Reticulated ceramic foams are used in many industrial processes involving fluid transport. High pore volumes, low pressure drops during fluid flow, good heat conductivity and mass transfer make them suitable for the application of

heterogeneous catalysis and filtration.<sup>1-4</sup> Examples include Pt<sup>1</sup> and Rh<sup>5</sup> based catalysts supported on cordierite and alumina foams, respectively. Alumina is low cost material with good mechanical properties and good resistance at rigorous process conditions, such as steam reforming.<sup>6</sup>

Nickel based catalysts supported on ceramics are applied in a variety of catalytic processes, e.g. ethanol steam reforming for the production of H<sub>2</sub> or H<sub>2</sub>/CO mixture (synthesis gas) and carbon nanotubes synthesis. Ni is effective substitute for high cost noble metals and it is recommended for industrial application. It has good selectivity towards hydrogen production.<sup>7, 8</sup> Nowadays, conventional routes for synthesis of catalysts include mixing and neutralization of precursor salts solutions or contacting the ceramic support with the impregnating solution. Precursor salts are transferred into suitable mixture of oxides by calcination. The catalyst is activated by hydrogen reduction, where only active component is transferred to metallic state.<sup>9</sup> Novel methods involve calcination of ultrasonically generated aerosols consisted of precursor salts solutions. They enable formation of fine spherical catalyst particles, precise stoichiometry control and high purity of products.<sup>10, 11</sup> There is a possibility of energy consumption savings and economic benefits if the calcination step is avoided during the production.

The aim of the present research was the optimization of the synthesis process of nanostructured Ni based catalyst supported on reticulated alumina-mullite foam, assisted by ultrasonic generated aerosol coating. The aerosol of NiCl<sub>2</sub> water solution was applied to alumina-mullite foam at elevated temperatures. The low-temperature reducibility of dried samples with chloride precursor and of calcined samples with oxide precursor was compared. It was determined that nickel compounds in all samples were reduced with high degree. The procedure resulted in homogeneous dispersion of Ni on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite surface. In the proposed synthesis route the calcination step was avoided, which contributed to the economic and technological efficiency of the catalysts production. Ni particles were mainly sintered during the reduction process. Therefore, a lower sintering temperature is to be investigated further.

## **Experimental section**

In order to economically enhance the synthesis of nanostructured Ni/Al<sub>2</sub>O<sub>3</sub> catalyst supported on reticulated ceramic foam assisted by aerosol coating, two experimental procedures were conducted and the synthesis process was optimized. Oxide precursor for the production of catalysts was obtained by calcination of Al<sub>2</sub>O<sub>3</sub> foam coated by NiCl<sub>2</sub> at 773 K for 1 h and the chloride precursor was obtained by drying Al<sub>2</sub>O<sub>3</sub> foam coated by NiCl<sub>2</sub> at 473 K for 1 h. Thin layers of NiO and NiCl<sub>2</sub> particles were deposited on alumina-mullite foam. Afterwards, the effectiveness of the hydrogen reduction on a low temperature was investigated.

Ultrasonic nebulizer (Profi Sonic, Prizma) with 1.7 MHz resonator frequency was attached to a tubular quartz reactor set in an electro resistant furnace (Fig. 1). A predetermined amount of NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in distilled water to achieve Ni to alumina-mullite ratio of 20 mas.%. The Ni<sup>2+</sup> ion concentration was 0.15 mol/L. The first experimental procedure involved the calcination of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite foam

(Sivex A40, Pyrotek) coated with  $\text{NiCl}_2$  by using ultrasonically generated aerosol of the solution at 773 K for 1 h.  $\text{NiCl}_2$  was transferred to  $\text{NiO}$ . The second procedure involved the drying of  $\alpha\text{-Al}_2\text{O}_3$ -mullite foam coated with  $\text{NiCl}_2$  at 473 K for 1 h. The latter procedure enabled the drying of samples without oxidation. Obtained samples were reduced by hydrogen at 633 K for 90 minutes, with the hydrogen flow rate of 20 L/h.

The microstructure of oxide precursors and samples obtained by the reduction of both oxide and chloride precursors was investigated using a JEOL SEM JSM 5800 scanning electron microscope (SEM). Microstructure represents correlation between the production technology and properties. The chemical composition of the reduced samples was investigated by XRD.

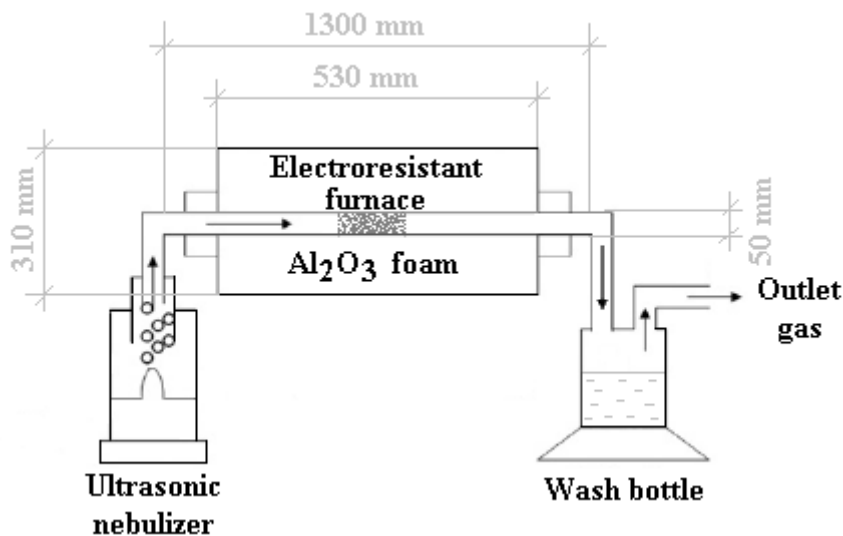


Figure 9. Set-up of aerosol assisted coating experiment

## Results and discussion

The aerosol assisted coating process was successful in all experiments. Alumina-mullite foam was uniformly covered with nickel coating after the reduction. Photographs of un-coated alumina-mullite foam and the nickel-coated foam are presented in Fig. 2.

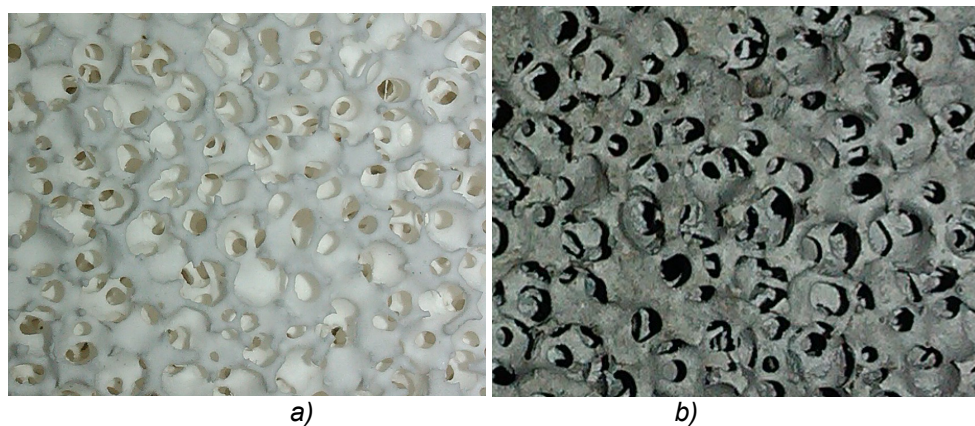


Figure 10. Photographs of a) alumina-mullite foam, b) Ni-coated alumina-mullite foam

SEM analysis of the strut surface of the calcined sample clearly indicates presence of NiO sponge-like agglomerates consisted of particles between 100 and 200 nm in diameter on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite surface (Fig. 3). The agglomerates were about 1  $\mu$ m in diameter. The faceted surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite is also clearly visible.

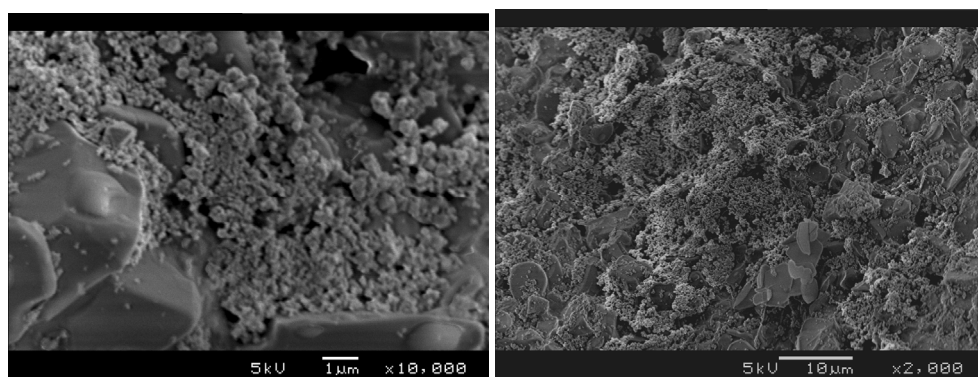


Figure 11. SEM of NiO supported on alumina-mullite foam, obtained by calcination at 773 K for 1 h

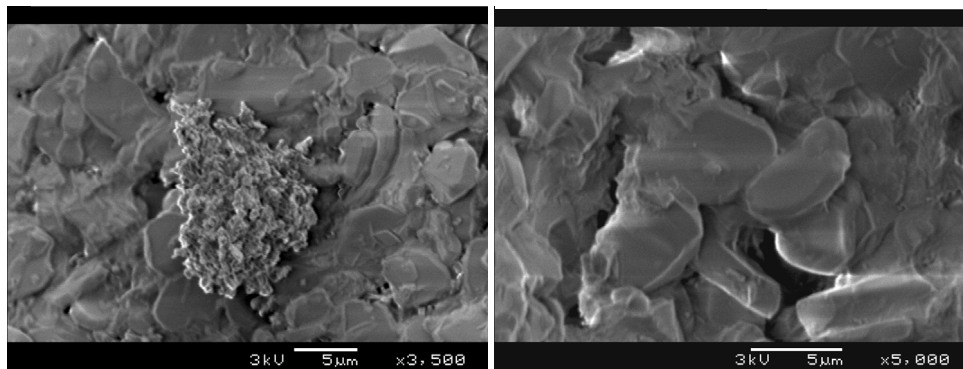


Figure 12. SEM of Ni supported on alumina-mullite foam, obtained by reduction of a) NiO calcined at 773 K and b) dried NiCl<sub>2</sub>, reduced at 633 K for 90 minutes

SEM of samples reduced at 633 K, obtained from oxide and chloride precursor, is presented in Fig. 4. Solid-state reactions between the catalytically active component and the carrier, i.e. ion adsorption reactions of the active component on the support that occurred during the reduction process at 633 K ensured the formation of the final structure of the catalyst (Fig. 4.b). Sponge-like agglomerates were present on the sample obtained by the reduction of NiO, Fig. 4.a. The presence of agglomerates is undesirable because it impairs the catalytic activity and leads to abrasion of the coating in a gas stream. Compared to that, the samples obtained by NiCl<sub>2</sub> reduction had smoother surface, with homogeneously dispersed active component, without detected agglomerates.

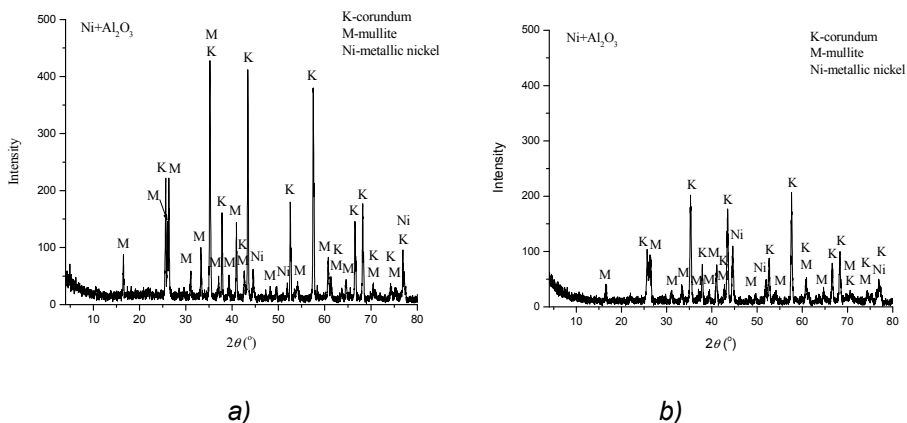


Figure 13. XRD of Ni supported on alumina-mullite foam after a) NiCl<sub>2</sub> and b) NiO reduction at 633 K for 90 minutes

XRD analyses clearly indicate that the residual NiO and NiCl<sub>2</sub> phases, as well as NiAl<sub>2</sub>O<sub>4</sub>, were not detected after the reduction (Fig. 5). In all samples, alumina, mullite and metallic nickel phases were detected, which indicates that the transferring of inactive form of the catalyst to its active form was complete. Intensity

of peaks, corresponding to metallic nickel, was higher in the sample obtained from chloride precursor. The most probable reason for the high degree of low-temperature reduction was the formation of thin film containing of nickel precursors. SEM of NiO supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite foam shows that nanoscale NiO particles were not uniformly distributed on the ceramic surface. Compared to mentioned, Ni particles obtained by reduction of NiCl<sub>2</sub> were more homogeneously dispersed and formed smoother metallic coating on the surface of ceramic foam. Based on the obtained results, it can be concluded that the catalysts can be synthesized by the direct reduction of NiCl<sub>2</sub> coated alumina-mullite foam, where the calcination step is avoided. The proposed process is more favourable from the technological and economic aspect. Considering that the the reduction was most probably complete at 633 K, a lower reduction temperature is proposed for further investigations.

## **Conclusions**

In the present research, the synthesis process of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by aerosol assisted coating was optimized. The low-temperature hydrogen reduction of NiO and NiCl<sub>2</sub> supported on reticulated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite foam was investigated. Based on the XRD and SEM analyses, it was concluded that the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were successfully synthesized from chloride precursor and the catalytically active component was homogeneously dispersed on the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-mullite foam. SEM analysis of calcined samples showed the presence of sponge-like agglomerates, which are undesirable because they impair the catalytic activity. Obtain results indicate that the calcination step can be avoided, that is, the direct reduction of chloride precursor after the ceramic foam impregnation with NiCl<sub>2</sub> aerosol and drying is sufficient for the synthesis of the catalysts. Proposed method can significantly contribute to the economic efficiency of the catalyst production process, as well as the production efficiency. Further research will be focused on the study of solid-state reactions between the catalytically active component and the carrier, i.e. ion adsorption reactions of the active components on the carrier, which enable the formation of the final homogeneous catalyst's structure at lower temperatures, in order to obtain the catalysts with service properties.

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