Material characterization of Au/Ni nanocatalyst for low-temperature carbon dioxide methanation

Błażej Tomiczek¹, Marek Szindler ¹, Mirosława Pawlyta¹, Paulina Boryło¹
¹Department of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Str. 44-100, Gliwice, Poland
E-mail: blazej.tomiczek@polsl.pl

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Abstract. The nanocatalyst for the carbon oxide methanation process is used, among others, in environmental protection, chemical industry, and renewable energy sources. The use of a suitable catalyst allows a chemical reaction to be carried out between unreacted gaseous substrates. The most frequently studied monometallic catalysts are: Ni, Ru, Rh, Pt, Au, Cu, Fe. Bimetallic nanocatalysts are equally popular. Their catalytic properties differ from those of pure component metals. Numerous studies indicate a positive effect in catalysts containing particles: Au-Ag, Au-Pt, Au-Pd, Pd-Ni, Pd-Cu. A review of the literature indicates that examples of the use of metal nanoparticles of spherical shape deposited on a nickel substrate in the methanation process are known, but so far no attempt has been shown in publications to produce a catalyst based on gold nanoparticles with developed surface in the form of spiky (nanourchins, nanostars) on a nickel base as presented in the article. Gold nanourchins are deposited on a nickel substrate in the form of a nickel molecular mesh. The prepared nanocatalyst has been subjected to structural analysis using a transmission electron microscope (TEM). Scanning Electron Microscopic (SEM) images were taken with a Zeiss Supra 35. Qualitative studies of chemical composition were also performed using the Energy Dispersive Spectrometer (EDS). Based on the TEM results, the appearance of the X-ray diffraction pattern was computer modelled. A nanocatalyst was obtained with a high coverage of the nickel molecular mesh surface with gold nanoparticles not exceeding 50 nm in diameter.

1 Introduction
Nanoparticles are defined as structures up to 100 nm in diameter [1-3]. They often exhibit unique physical, chemical, and biological properties that differ significantly from their macroscale forms. Nanoparticles are characterized by a specific geometric structure characterized by a high surface area to volume ratio, which is inversely proportional to the particle diameter. This causes a significant increase in their activity and affects the absorption properties and reactivity [1-5]. The reduced size changes the total energy of the system responsible for thermodynamic stability, which is the result of disturbances in the wave function of the electrons. The area of nanoparticles applications is still growing. On the priority list of nanomaterials predicted, the largest commercial use in the near future, published as part
of the work carried out in the OECD (Inter-Organization Program for the Sound Management of Chemicals - IOMC), the following metals and their oxides have been placed: silver, iron, aluminum, cerium, titanium, zinc or nickel [4-7]. Nanoparticles are used, among others in the cosmetics, pharmaceutical, automotive and chemical industries (composites, paints, varnishes), construction, electronics, biomedicine and bioengineering, environmental protection and many others [1-3]. Metal nanoparticles in particular are of great interest to researchers due to their unique physicochemical properties determined by their size. They can significantly increase the speed, selectivity, and efficiency of chemical processes while minimizing the amount of by-products when they act as a catalyst. The most intensively studied monometallic catalysts are: Ni, Ru, Rh, Pt, Au, Cu, Fe [8-12]. Bimetallic nanocatalysts are equally popular. Their catalytic properties differ from those of pure component metals. The use of bimetallic nanocatalysts with an appropriate carrier is designed to eliminate the problem of the possibility of blowing out nanoparticles with catalysis products. Numerous studies indicate a positive effect of catalysts containing particles: Au-Ag, Au-Pt, Au-Pd, Pd-Ni, Pd-Cu [9-15]. A review of the literature indicates that examples of the use of metal nanoparticles of spherical shape deposited on a nickel substrate in the methanation process are known, but so far no attempt has been shown in publications to produce a catalyst based on gold nanoparticles with developed surfaces in the form of spikes (nanourchins, nanostars) on a nickel base as presented in the article. Among the various geometries of gold nanoparticles, gold nanourchins, alternatively referred to as nanoflowers, nanostars, or multibranched gold nanoparticles, have received much attention in recent years [16-17]. This is because of their catalytic activity, molecular detection, and biological applications in immunoassays, dark field imaging of cells and in plasmonic biosensors.

2 Material descriptions and research methodology

Two groups of methods can be distinguished in the synthesis of nanourchins: the seeded-growth and non-seeded-growth methods. In this article, gold nanourchins synthesized by the method described by Weifeng Lv [17] were used to produce the Au /Ni nanocatalyst. It’s non-seeded method in which as a source of gold, Tetrachloroauric (III) acid trihydrate (HAuCl₄·3H₂O, 99.5%) was used. Ascorbic acid was used as a reducing agent. Then the ready nanourchins was suspended in phosphate buffered saline (PBS). The synthesized nanoparticles were deposited directly on a nickel substrate in the form of a molecular mesh (Figure 1).

![Figure 1. Nickel molecular mesh](image)

Scanning electron microscopic (SEM) images were taken with a Zeiss Supra 35. The accelerating voltage was 5 kV. To obtain images of the surface topography, the detection of secondary electrons (by the detector In Lens) was used. Qualitative studies of chemical composition were also performed using the energy-dispersive spectrometer (EDS). The prepared nanocatalyst has been subjected to structural analysis using a transmission electron microscope (TEM). High-resolution transmission electron microscopy (HR-TEM) analysis was carried out using a transmission electron microscopy/scanning
transmission electron microscopy (TEM/STEM) system (Titan 80-300, FEI Company, Hillsboro, Oregon, USA) with a super twin-lens operated at 300 kV and equipped with an annular dark field detector. The crystal structures and diffraction patterns of nanoparticles were simulated using VESTA software.

3 Results and Discussion

Clusters of palladium nanoparticles on most of the nickel surface were recorded. As can be seen from the image, there is a size distribution of particles below 50nm. However, there is a high preference for very small clusters (Figure 2).

An EDS analysis was performed, recording the reflection characteristics of gold and nickel (Figure 3). For gold, 2.203 eV (spectrum line M$_{β1}$) were registered. For nickel, 0.866 eV (spectrum line L$_{β1}$), and 7.480 eV (spectrum line K$_{α1}$) were registered.

![Figure 2. SEM surface topography images of the Au-Ni nanocatalyst with gold nanourchins](image)

![Figure 3. EDS spectrum of the Au-Ni nanocatalyst with gold nanourchins](image)
Detailed results of surface morphology and structural studies were performed using the S/TEM. For research purposes, the STEM imaging mode was used. The Titan 80-300 microscope is equipped with three coaxial detectors dedicated to STEM mode: Bright Field–BF, Annular Dark-Field–ADF and High-Angle Annular Dark-Field–HAADF (Figure 4). The SAED pattern shows a clear appearance of diffraction rings from the Au. To solve the SAED pattern, JCPDS files were used, according to which were assigned the appropriate Miller indices (Figure 5b). The crystal structure of the gold nanoparticle was identified as face-centered cubic (Figure 6a). Based on the TEM results, the appearance of the X-ray diffraction pattern was computer modelled. Specialist VESTA software was used for this purpose. It is a 3D visualization program for structural models, volumetric data such as electron/nuclear density, and crystal morphology. VESTA allows to simulate X-ray and neutron powder diffraction patterns from lattice and structure parameters. The simulated diffraction pattern of gold nanoparticles is shown in Figure 6b. Lattice parameters which was used for simulation of diffraction pattern is collected in Table 1.

Table 1. Lattice parameters used for simulation of gold nanoparticle diffraction pattern [18]

| Crystal system: | Cubic | No. | h | k | l | d [Å] | 2Theta[deg] | I [%] |
|-----------------|-------|-----|---|---|---|-------|------------|-------|
| Space group:    | F m -3 m | 1 | 1 | 1 | 1 | 2,35039 | 44,739 | 100,0 |
| a (Å):          | 4.071 | 2 | 0 | 0 | 2 | 2,03550 | 52,138 | 48,4 |
| b (Å):          | 4.071 | 3 | 0 | 2 | 2 | 1,43932 | 76,848 | 29,8 |
| c (Å):          | 4.071 | 4 | 1 | 1 | 3 | 1,22745 | 93,563 | 34,0 |
| Alpha (°):      | 90,0  | 5 | 2 | 2 | 2 | 1,17520 | 99,132 | 9,8  |

Figure 4. The BF_DF (a) and HAADF (b) images of Au-Ni nanocatalyst with gold nanourchins registered in STEM mode
4 Conclusions

Review of the literature indicates that there are known examples of the use of spherical-shaped metal nanoparticles deposited on a nickel substrate in the methanation process, but so far no attempts have been made in the publications to produce a catalyst based on gold nanoparticles with a developed surface in the form of spiked nanostars (nanourchins) on a nickel substrate. In summary, we prepared nano Au supported by Ni molecular mesh. By using electron transmission microscopy and XRD simulation, the phases in the nanocatalyst were identified. A nanocatalyst was obtained with a high coverage of the nickel molecular mesh surface with gold spiked from nanoparticles not exceeding 50 nm in diameter. The results obtained by the authors of this paper provide a promising perspective for research and indicate that this is an attractive direction in the search for new solutions in environmental protection, chemical industry, and renewable energy sources.

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