Core-shell composite metal catalysts incased into natural ceramic nanotubes

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Abstract. The bimetallic halloysite nanotubes were prepared by the injection of halloysite-containing aerosols into the microwave plasma reactor. Nanotubes contain metal nanoparticles formed from the metal salt solution in the lumen of nanotubes and the iron oxide nanoparticles at the outer surface of nanotubes. Such halloysite composites may be sputtered onto the surface of the porous carrier forming the nanostructured catalyst, as was shown by the pure halloysite sputtering onto the model porous ceramic surface.

1. Introduction
Nanotubes of different nature intercalated with metal and metal oxides are very efficient as mesoporous media for advanced catalysis. Natural halloysite clay nanotubes available in large quantities at low price are very promising for this purpose. Halloysite tubes have diameter of around 50 nm, inner lumen of 15-20 nm and length of 1-2 μm [1]. Traditional intercalation method usually include wetting nanotubes with aqueous metal salts following with chemical treatment for reduction [2,3]. The reaction volume being restricted within nanoscale, one can produce metal nanoparticles fitting the tube lumen exploiting such tubule nanoreactor. Previously, we have applied this approach for the synthesis of 5-10 nm diameter particles of Ag, Au and Fe3O4 incased into such core-shell structures [4].

2. Experimental
In the present work, even better results on core-shell nanocatalytic systems were obtained by introducing the aerosols of aqueous nitrate salts of iron, nickel or cobalt mixed with the clay nanotubes into the low temperature argon or carbon dioxide plasma. Treatment was performed during 2 sec preventing the halloysite decomposition though allowing for metal nanoparticle formation on and into the tubes.

The microwave plasma reactor was assembled from coaxial waveguide with the central nozzle electrode and the magnetron (P=1 kW, ν=2.45 GHz). The high electromagnetic field density near the
nozzle electrode opening ensures the ionization of the wide range of gases (air, argon, nitrogen, methane, carbon dioxide, etc.). The energy conversion efficiency by the reactor is up to 60%, while the plasma temperature is ca. 2500 K.

3. Results and discussions
The iron oxide nanoparticles formed in the tube lumen have diameter of ca. 3 nm and nanoparticles formed on the tube outer surface have larger diameters of ca. 10 nm (see figure 1). The reason of this diameter difference may be related with steric hindrance, different component concentrations inside and outside the nanotube, as well as with the different chemistry and the possible temperature gradient in the tube interior and outer surface.

![Figure 1](image1.png)

**Figure 1.** TEM micrograph of the CoO nanoparticles in the interior and Fe$_2$O$_3$ at the outer surface of halloysite tube.

The elaborated method allowed the deposition of different metals at the inner and outer surfaces of ceramic nanotubes. As the outer layer of metal nanoparticles is formed from the eroded iron nozzle electrode material, spraying of the aerosols of cobalt nitrate-loaded halloysite into the microwave plasma produces bimetallic core-shell nanotubes.

In the present work, there was made an attempt to sputter pure halloysite on a porous ceramic surface by direct aerosol injection of its aqueous suspension in plasma beam. An even nanoparticles layer thicker than 10 μm was formed on a ceramic surface as a result. SEM micrographs show that halloysite particles do not lose their shape and do form an even close-packed layer on a surface of the porous catalyst support in microwave plasma conditions, as one can see in figure 2.

![Figure 2](image2.png)

**Figure 2.** SEM micrographs of the same ceramic surface before (at the left) and after (at the right) the plasma sputtering with halloysite.

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The proposed method of halloysite sputtering on a solid porous surface may be implemented for the advanced nanostructured catalysts preparation, given the possibility of preliminary preparation of the bimetallic core-shell halloysite nanotubes. This approach is quite perspective for the preparation of new high-efficiency catalysts for the organic and petrochemical syntheses.

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