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IN-SITU SCHIFF BASE ASSISTED SYNTHESIZE OF METAL NANOPARTICLES INSIDE HALLOYSITE NANOTUBES

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Nowadays, scientific interest on the application of natural nanomaterials like nanoclays has increased. Halloysite nanotubes are ones of the promising naturally occurring nanotubes due to its unique multiwall tubular structure and mesoporous lumen that vary from 15 to 50 nm. The low price and biocomparability of halloysite make it much more interesting for the industry than expensive synthetic nanomaterials like carbon nanotubes. It has already been shown that halloysite is a good support material for nanoparticles. Seeding metal nanoparticles like Au, Pt, Pd, Ag nanoparticles on the halloysite outer surface has been widely reported but only a few works are dedicated to metal loading inside halloysite lumen [1-2].

Here we report a preparation method of metal nanoparticles assembled in the lumen of halloysite nanotubes (HNTs). Metal-nanoparticles were synthesized inside HNT lumen by the ligand assisted intercalation technique followed by in-situ reduction of metal complexes with $NaBH_4$. Schiff base was chosen as loading agent as it is an effective ligand for stable metal complexes formation. To investigate the efficiency of Schiff base assisted metal salt loading into HNTs we performed an on-line light adsorption experiment for ruthenium chloride ethanol solution. The pristine HNTs showed zero adsorption of ruthenium chloride and HNTs-Schiff base composite showed rapid adsorption of metal salt with time. The morphology and element composition of halloysite/metal nanoparticles composites were analyzed with a transmission electron microscope (TEM) and energy-dispersive X-ray spectrometry analysis (EDX).

Proposed method allow reaching a high yield of nanotubes intercalated with metal nanoparticles (Rh, Ru, Pt, Cu etc.) using low concentration of metal salts. This is the efficient method for synthesize of halloysite based nanocatalysts with nanoparticles inside halloysite lumen prevented from aggregating.

1. Noelia M. Sanchez-Ballester, et al. *J. Mater. Chem. A*, 3, 6614–6619, 2015, “Activated interiors of clay nanotubes for agglomeration-tolerant automotive exhaust remediation”.
2. V. Vinokurov, et al. ***Sci. Technol. Adv. Materials*****,** v.18, published on line, 2017, “Formation of Metal Clusters in Halloysite Clay Nanotubes,” http://dx.doi.org/10.1080/14686996.2016.1278352

This work was supported by the Ministry of Education and Science of the Russian Federation (Grant № 14.Z50.31.0035). The work of P. A. Gushchin and E. V. Ivanov is funded by the President of Russia (grants MK-3299.2017.8).