CATALYTIC ACTIVITY OF HALLOYSITE BASED Ru/Rh NANOCATALYSTS IN HYDROGENATION OF PHENOL

87

Glotov A.P.[1,2], Chudakov Y.A.[1], Stavitskaya A.V.[1], , Zolotukhina A.V.[2], Vinokurov V.A.[1], Maksimov A.L.[2], Lvov Y.M.[1,3]

[1]Gubkin Russian State University of Oil and Gas, Leninskiy prospect 65, Moscow, 119991, Russia

[2]Lomonosov Moscow State University, Chemistry Department, Leninskiye Gory 1-3, GSP-1, Moscow, 119991, Russia

[3]Louisiana Tech University, Ruston, LA 71272, U.S.A.

Alex.glotov@aol.com

Halloysite nanotubes 0.2–2 mm in length, 40–70 nm in outer diameter and 10–30 nm in inner diameter, as two-layered aluminosilicate clay, have exhibited promising results as a catalyst support due to their inherent hollow nanotube structure and different outside and inside chemistry [1, 2].

Here we report a new efficient halloysite based nanocatalysts with Ru and Rh nanoparticles assembled in the internal cavity of halloysite. Ru and Rh nanoparticles were synthesized using ligand assisted metal salts intercalation techniques followed by in-situ reduction with $NaBH_4$. First Schiff base composed of furfural and hydrazine was synthesized inside halloysite cavity. Halloysite with Schiff base inside was loaded with Ru or Rh chloride from ethanol solutions (1 mg/ml) via formation of Schiff base-metal chloride complexes. After The Schiff base-metal chloride complexes were reduced with $NaBH_4$ to form Ru or Rh nanoparticles with the size from 1 to 5 nm deposited inside halloysite nanotubes, the catalytic activity of synthesized nanocatalysts was studied in a reaction of phenol hydrogenation.

All samples were characterized by IR and ^{27}Al NMR spectroscopies, low-temperature adsorption/desorption of nitrogen, and XPS techniques. The formation of metal nanoparticles in the internal cavity of halloysite was proved by TEM. Metal content was determined by X-ray fluorescence spectroscopy. According to XPS data, metal nanoparticles are preferably in the zero valent state.

Catalytic hydrogenation of phenol was carried out in a stainless steel 40 ml Parr batch reactor heated in a temperature-controlled oven. In a typical experiment, 300 mg of a phenol and 300 µl of water were placed to the reactor. Next, 5, 10 and 15 mg of Ru/halloysite or Rh/halloysite (metal content 1 %wt) was added. The reactor was sealed at the H_2 pressure of 3.0 MPa and heated to the reaction temperature (80 ºC). It was shown, that in the case of Rh/halloysite catalyst (15 mg) and reaction time 6 hours phenol conversion reached to 100% with cyclohexanol selectivity 81 %. Decrease the quantity of Rh/halloysite catalyst to 5 mg leads to decreasing phenol conversion to 78 % with higher cyclohexanol selectivity (99 %). Ru/halloysite catalyst (15 mg) is more active in hydrogenation of phenol. Thus, conversion of phenol in this case is 83% and cyclohexanol selectivity 100 %. Reduction of Ru/halloysite catalyst content to 5 mg leads to a significant diminution of phenol conversion (63 %) while cyclohexanol selectivity retains.

1. Y. Zhang, A. Tang, H. Yang, J. Ouyang. Applied Clay Science 119 (2016) 8–17.
2. A. Filippov, D. Afonin, N. Kononenko, Y. Lvov, V. Vinokurov. Colloids and Surfaces A: Physicochemical and Engineering Aspects, Available online 30 August 2016.

This work was supported by the Ministry of Education and Science of the Russian Federation (Grant № 14.Z50.31.0035)