

NANOSTRUCTURED CORE-SHELL RUTHENIUM CATALYSTS FOR AROMATICS HYDROGENATION

Glotov A.P.¹, Chudakov Y.A.¹, Nedolivko V.V.¹, Zasyalov G.O.¹, Vinokurov V.A.¹

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

e-mail: glotov.a@gubkin.ru

The quality of motor fuels is an important factor for environmental safety. In order to satisfy ecological restrictions, refineries are forced to reduce the amount of benzene and aromatics in fuels [1]. All these components contain a different amount of aromatic compounds, the qualitative composition of which is not the same for each fraction. In most cases, the limiting content of these compounds is significantly exceeded the norm. In this regard, various hydrogenation processes are used at the plants, aimed at reducing the concentration of aromatic substances in the composition of commodity fuels. These processes take place in the presence of heterogeneous metal-based catalysts. The effectiveness of the application of a particular type of catalyst is determined by the properties both of the carrier and active metal. Various carriers, such as alumina, silica, cerium and titanium oxides for hydrogenation catalysts of aromatic compounds are used [2].

In this work, catalysts based on halloysite nanotubes modified with organo-silanes of different structures with ruthenium nanoparticles were synthesized and tested in benzene, toluene and ethyl benzene hydrogenation. Halloysite is a natural mineral from the kaolin group with the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, $n = 0, 2$, represents aluminosilicate nanotubes with a length of 0.5–2 μm and outer and inner diameters of 40–60 and 10–30 nm, respectively [3].

The synthesized catalysts were characterized by nitrogen low-temperature adsorption/desorption (NLTAD), H₂-temperature programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS). The formation of metal nanoparticles in the internal cavity of halloysite was proved by transmission electron microscopy (TEM).

Catalytic hydrogenation of aromatics was carried out in a stainless steel 40 ml Parr batch reactor heated in a temperature-controlled oven. In a typical experiment, 1.5 ml of a substrate with water or not was placed into the reactor. Next, 5, 20 or 40 mg of Ru/halloysite (metal content 2 %wt) was added. The reactor was sealed at the H₂ pressure of 3.0 MPa and heated to the reaction temperature (80 °C).

It was shown that the preliminary modification of halloysite nanotubes with organo-silanes changes the charge of the outer surface of aluminosilicate and facilitates the intercalation of ruthenium nanoparticles into lumen of nanotubes. The catalysts synthesized show high activity in the model reaction of benzene hydrogenation to cyclohexane in both aqueous and organic media with TOF's about 80 000.

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REFERENCES

1. L. Peyrovi M.H., Rostamikia T.A., Parsafard N.B. // *Energy and Fuels*. 2018, V. 32:11, pp. 11432-11439.
2. Dwivedi A.D., Rai R.K., Gupta K., Singh S.K. // *ChemCatChem*. 2017, 9, 1930.
3. Glotov A., Stavitskaya A., Chudakov Ya., Ivanov E., Huang W., Vinokurov V., Zolotukhina A., Maximov A., Karakhanov E., and Lvov Yu. // *Bulletin of the Chemical Society of Japan*. 2019, 92:1, 61-69.