

Benzene Hydrogenation over Ruthenium Catalysts Supported on Aluminosilicate Nanotubes

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The hydrogenation of aromatic compounds is one of the most important areas of modern petroleum chemistry. The hydrogenation of benzene yields cyclohexane, which is used in the production of caprolactam, cyclohexanol, and adipinic acid and as a solvent. The reaction is run both in the liquid and gas phases using transition-metal catalysts, with particular attention being paid to ruthenium. Traditionally, alumina, silica, titania, activated carbon, and synthetic and natural aluminosilicates are used as catalyst supports.

In this study halloysite was used as a support. Halloysite represents natural multilayer nanotubes with the outer negatively charged surface composed of silica and the inner positively charged surface composed of alumina. This difference in the chemical compositions and electrochemical charges of the inner and outer surfaces in combination with the mesosized inner space open wide opportunities for the selective modification of halloysite nanotubes (HNTs) to impart the desired properties to them [1].

Ru-containing catalysts based on aluminosilicate (HNTs) are synthesized by preliminary functionalization of the support surface by aminopropyltriethoxysilane (APTES) followed by the microwave-assisted deposition of ruthenium to provide the intercalation of metal nanoparticles into the inner space of nanotubes [2]. The composition and structure of the synthesized catalysts are studied by X-ray fluorescent analysis (XRF), low-temperature nitrogen adsorption/desorption, transmission electron microscopy (TEM), and hydrogen temperature-programmed reduction (TPR-H₂).

To impart new properties to nanotubes, specifically hydrophobicity, they were modified with APTES, which leads to charge exchange between inner and outer surfaces of nanotubes, as evidenced by a change in the ξ potential of the outer surface from – 52 to 6 mV. Formation of the active phase is considerably affected not only by the support type but also by the technique of metal deposition. Impregnation of the support with an aqueous solution of ruthenium salt was assisted by microwave radiation. This technique provides a more uniform deposition of the metal on the support surface compared with the standard impregnation method. According to elemental analysis, the content of ruthenium in catalysts Ru/HNT and Ru/HNT-m after their reduction by sodium borohydride ensuring the transition of ruthenium to the zero-valence state is 1.5 and 2.0 wt %, respectively. Reduction in specific surface area and pore volume and diameter upon ruthenium deposition, especially in the case of catalyst Ru/HNT-m, in which the content of the active component is higher than that in the Ru/HNT sample, may be explained by the formation of metal particles on the inner and outer surfaces.

Microwave-assisted impregnation of supports with the aqueous solution of ruthenium salt makes it possible to obtain a fine catalyst with metal nanoparticles uniformly distributed on the support surface, as indicated by the TEM data. The microwaveassisted deposition of

ruthenium on the initial halloysite surface yields a fine phase of ruthenium nanoparticles with a diameter of ~ 1.3 nm, mostly on the outer surface of halloysite nanotubes. Because the inner surface is charged positively, ruthenium cations cannot intercalate into the inner cavity, but they predominantly interact with the negatively charged outer surface.

In the case of the APTES-modified catalyst, ruthenium nanoparticles are intercalated predominantly into the inner space of halloysite. For material Ru/HNT-m, there is a bimodal size distribution of metal particles with maxima at 0.9 and 1.3 nm. A smaller size corresponds to particles adsorbed on the inner surface; a larger size corresponds to particles adsorbed on the outer surface.

The generation of ruthenium nanoparticles both in the inner cavity and on the outer surface of the modified support is also confirmed by the TPR- H_2 studies. The TPR- H_2 profile obtained for Ru/HNT-m shows peaks at 139 and 161°C corresponding to the reduction of ruthenium oxides RuO_x and RuO_2 fixed on the material surface and in the inner cavity of HNTs [3]. In the case of Ru/HNT, there is only one peak of hydrogen absorption with a maximum at 139°C assigned to the reduction of RuO_2 to Ru0. This observation suggests that the uniform fine layer of ruthenium nanoparticles is formed on the surface of halloysite and agrees with the TEM data. A wide shoulder in the range of 200–260°C may be attributed to the reduction of ruthenium oxides and oxochloride strongly bound to the support surface.

In accordance with the TPR- H_2 data, the content of ruthenium in Ru/HNT and Ru/HNT-m is 1.2 and 1.9 wt %, respectively, in agreement with elemental analysis. Note that for catalyst Ru/HNT-m the most pronounced hydrogen absorption is observed at 161°C (0.220 mmol/g). This finding confirms formation of ruthenium nanoparticles in the inner cavity of nanotubes; their content attains 1.1 wt %.

The activity of the catalysts in benzene hydrogenation at a temperature of 80°C and a hydrogen pressure of 3 MPa both in the hydrocarbon medium and in the twophase system with water is studied. It is shown that, in the presence of water, the hydrogenating activity of the catalyst based on modified halloysite nanotubes is considerably higher than that of the sample prepared using the initial halloysite as a support. For example, in the two-phase system in the presence of water, both catalysts show a fairly high activity during the first 20 min: the conversion of benzene is on the order of 30–40%. In hydrogenation catalyzed by Ru/HNT-m, the substrate conversion attained during 90–150 min is as high as 92%. For Ru/HNT, this parameter does not exceed 40%.

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References:

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