CATALYTIC ACTIVITY OF Ru-CONTAINING HALLOYSITE CATALYSTS IN HYDROGENATION OF AROMATIC COMPOUNDS UNDER TWO-PHASE CONDITIONS

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Halloysite is environmentally friendly, natural and cheap tubule nanomaterial available in thousand tons. Halloysite nanotubes are formed by 10-15 revolution of kaolin alumosilicate sheets and have diameter of 50-60 nm, a lumen of 12-15 nm and length of 500-800 nm. Halloysite surface is SiO_2 and the tube inside is Al_2O_3 which are oppositely (positive / negative) charged at pH range of 3-9 [1]. Due to its tubular structure, halloysite could be used as a container for stable metal nanoparticles and its side dependent chemistry make it a perfect material for modification.

In this work we compare two types of halloysite based Ru-nanocatalysts (Ru/halloysite; M-Ru/halloysite) with Ru nanoparticles assembled inside halloysite nanotubes in reaction of aromatic hydrocarbon hydrogenation under two-phase condition. Ru/halloysite was synthesized using pristine halloysite as a carrier and M-Ru/halloysite was synthesized using halloysite modified with cetyl trimethylammonium bromide. In both nanocatalysts Ru-nanoparticles were synthesized using Schiff base assisted metal salts intercalation techniques followed by in-situ reduction with $NaBH_4$ [2].

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 aromatic compounds was carried out in a stainless steel 40 ml Parr batch reactor heated in a temperature-controlled oven. In a typical experiment, 250 μl of aromatic compounds (benzene, toluene and ethylbenzene) and 250 μl of water were placed to the reactor. Next, 5 mg of Ru/halloysite or

M-Ru/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 °C). Reaction time = 1 hour. Halloysite based catalysts showed high activity in the hydrogenation of aromatic compounds in the presence of water. It was shown, that aromatic compounds conversion under two-phase conditions on the Ru/halloysite catalyst is 88 % with 96-100 % selectivity of each product: cyclohexane, methylcyclohexane and ethylcyclohexane. It was shown, that M-Ru/halloysite catalyst is more active in hydrogenation of aromatic compounds with the presence of water. Thus, conversion of aromatic compounds is higher and is about 99 % while maintaining products selectivity.

References

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