

Synthesis of bifunctional Ag–Pd@UiO-66 catalysts with different methods

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Catalytic conversion of biomass and products of its processing attracts growing attention due to limited traditional carbon sources such as fossil hydrocarbons. One of the main challenges of biomass valorization is the development of multifunctional catalysts, e.g., heterogeneous systems containing active sites with different nature for cascade-type reactions.

The aim of the present investigation is to develop the bifunctional catalyst with redox active species combined with Lewis acid active sites. This idea can be realized by application of metal–organic framework UiO-66 as a support-cocatalyst for Ag–Pd nanoparticles due to high concentration of Lewis acid active sites, high thermal, chemical and aqueous stability, large specific surface area and high pore volume [1]. UiO-66 is a porous zirconium terephthalate consisting of $Zr_6O_4(OH)_4$ octahedrons connected with terephthalic acid that forms a 3D porous network. A combination of Ag–Pd bimetallic nanoparticles as redox species and Lewis acids sites of UiO-66 has a great potential to produce an active catalyst for cascade-type reactions.

The most common approaches to immobilize metal nanoparticles in MOF are “ship in a bottle”, “bottle around a ship” and solution impregnation methods. All techniques have some drawbacks, including possibility of collapse of the MOF structure, pore space blocking or formation of large metal particles on the external surface of MOF particles.

Nowadays there are a few reports on immobilization of silver/palladium nanoparticles in MOFs. Metal nanoparticles prepared via “double solvent” approach had very small particle size [2]. Immobilization of silver nanoparticles in UiO-66 was realized via solution infiltration method [3], however, the final particle sizes were about 7–10 nm, which was much higher in comparison with pore sizes of UiO-66 (0.9 and 1.1 nm).

Immobilization of Ag–Pd nanoparticles was performed by different techniques, such as wetness impregnation of water or acetonitrile silver nitrate solutions and palladium nitrate/acetylacetonate solution, double solvent approach and self-developed wetness impregnation method with one-pot chemical reduction technique. The effect of impregnation technique on the catalyst structure and activity was tested by XRD, low-temperature nitrogen adsorption, DRS UV-vis and TEM methods. Catalytic properties were studied in aerobic oxidation of propylene glycol into lactic acid.

Bimetallic nanoparticles were successfully immobilized inside the pores of UiO-66 by “double solvent” and wetness impregnation methods with one-pot chemical reduction technique. Formation of small metal nanoparticles (<3 nm) was confirmed by XRD and TEM methods. Low-temperature nitrogen adsorption analysis showed that the large part of UiO-66 pore volume was still available for substrate. The use of acetonitrile solution of palladium acetylacetonate and silver nitrate instead of silver and palladium nitrates mainly led to formation of Ag and Pd monometallic particles, which was confirmed by DRS UV-vis and XRD methods. The influence of Ag/Pd ratio and reduction conditions will also be discussed.

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References

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