NANOCOMPOSITE OF Pd NANOPARTICLES WITH MIL-101(Cr) COORDINATION POLYMER FOR CATALYTIC HYDROGENATION OF QUINOLINE

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Reactions of catalytic hydrogenation of heterocycles are very important for modern organic chemistry and chemical manufacturing for synthesis of active pharmaceutical ingredients and compounds for agrochemistry. Pd-containing catalysts are widely used for such processes, and among them composites of porous coordination polymers (PCPs) with Pd nanoparticles (NPs) are considered as promising objects. The advantages of such systems include thermal and hydrolytic stability, as well as microporosity which prevents NPs agglomeration and can give rise to size-selectivity of the catalyst.

The aim of this work was the study catalytic activity of the nanocomposite of Cr(III) PCP $[Cr_3O(OH)(bdc)_3]_n$ (bdc^{2-} = 1,4-benzenedicarboxylate) with Pd NPs in quinoline hydrogenation reaction.

The composite was prepared by impregnation of the PCP, suspended in n-hexane, with water solution of H_2PdCl_4, followed by Pd(II) reduction to metal directly in pores. The volume of water phase was taken to be close to the pores volume of the PCP. As the result, H_2PdCl_4 solution was completely absorbed by the PCP, which minimized formation of Pd NPs on the "external surface" of PCP particles. The composites contained 10 % (by weight) of Pd. It was shown by transmission electronic microscopy that Pd NPs in the composite had spherical form and size *ca*. 2-4 nm.

It was found that the composites catalyzed hydrogenation of quinoline forming 1,2,3,4-tetrahydroquinoline. Catalytic hydrogenation was performed in different conditions at temperature varying from 50 to 150 ºC and H_2 pressure varying from 3 to 5 MPa. The products were analyzed by ^{1}H NMR spectroscopy and GC MS or HPLC. The yield of 1,2,3,4-tetrahydroquinoline at 5 MPa pressure and 150 ºC was almost 100 %, while it decreased to *ca*. 40 % upon pressure reduction to 3 MPa and temperature reduction to 50 ºC.