CATALYTIC ACTIVITY OF Cu(II) AND Fe(III) POROUS COORDINATION POLYMERS IN OXIDATION OF 1,2,3,4-TETRAHYDRO-1-NAPHTHOL BY HYDROGEN PEROXIDE

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Porous coordination polymers (PCPs) of 3d metals are considered as promising catalysts of oxidation reactions for fine organic synthesis. Use of such catalysts allows reactions carrying out in conditions of heterogeneous catalysis (including use of flow reactors), which simplifies separation of the catalyst and product purification. Determination of factors, which influence catalytic activity of such systems, is important task of modern physical chemistry and catalysis.

The aim of this work was to evaluate and to compare catalytic activity of PCP $Cu_3(btc)_2$ (known as HKUST-1; btc^{3-} is 1,3,5-bensenetricarboxylate) and $Fe_2(OH)_3(btc)$ in reaction of 1,2,3,4-tetrahydro-1-naphthol oxidation by hydrogen peroxide leading to α-tetralone (Fig. 1).

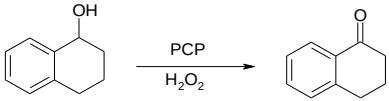

Fig. 1. Scheme of reaction studied

PCPs $Cu_3(btc)_2$ and $Fe_2(OH)_3(btc)$ were synthesized by electrochemical dissolving of metallic Cu or Fe anodes, respectively, in solutions containing H_3btc. Oxidation reactions were carried out by stirring of solutions, containing reagents and suspended catalyst, at 25 ºC for 24 h. Hydrogen peroxide was taken in excess, acetonitrile was used as solvent. The products were analyzed by ^1H NMR and HPLC.

It was found that $Fe_2(OH)_3(btc)$ was significantly more active compared to $Cu_3(btc)_2$; in similar conditions the yield of α-tetralone was significantly higher in the case of $Fe_2(OH)_3(btc)$. However, at high loading of $Fe_2(OH)_3(btc)$ oxidation did not stop on formation of α-tetralone but led to a mixture of products, resulting from hydrocarbon chain cleavage. In the case of $Cu_3(btc)_2$ pure α-tetralone could be isolated along with unreacted 1,2,3,4-tetrahydro-1-naphthol.

In order to perform the process in flow regime, composite of $Cu_3(btc)_2$ and aerosil was prepared by deposition of $Cu_3(btc)_2$ microparticles on aerosil (disperse SiO_2) under action of ultrasound in suspension. It was found that micropores volume of the composite decreased compared to pure $Cu_3(btc)_2$ proportionally to its content. Passing of the reaction mixture trough 2 cm layer of the composite led to significant increase of conversion compared to batch reaction. For example, the yield of α-tetralone after passing through a column was 33 % for 2 hours, while similar yield in batch was achieved after 24 h of reaction at similar concentrations of the reagents.