

THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

*Proceedings of
V International scientific school-conference for young scientists*

September 25-29, 2018

Tomsk 2018

Synthesis of hybrid materials N-hydroxyphthalimide@Co-MOF/SiO₂ as catalysts for oxidation of hydrocarbons

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Selective catalytic oxidation of hydrocarbons into value-added derivatives with dioxygen is a fundamental transformation in organic chemistry. However, still the activation of C–H bond and prevention of overoxidation is a challenging task. Generally, industrial catalysts employed in the liquid-phase oxidation of alkanes and cycloalkanes are homogeneous materials based on transition metal salts. Such processes produce a large amount of environmentally undesirable wastes and require complicated procedures for the catalyst separation and product purification. N-hydroxyphthalimide (NHPI) is known as a valuable catalyst for aerobic oxidation of various organic compounds [1]. Its activity is related to the formation of phthalimide N-oxyl (PINO) radicals that abstract hydrogen from the substrate. The PINO formation is usually facilitated by the additives of transition metals [2] such as, for example, Co(II) salts. In the present work we managed to synthesize heterogeneous catalyst that contains both Co(II) and NHPI through immobilization of NHPI into the pores of Co-based silica-supported metal-organic framework (MOF).

Two kinds of silica surface modification were used to build up Co-MOF on its surface: 1) deposition of Co-containing precursor through wetness impregnation method with aqueous Co(NO₃)₂ solution followed by calcination and 2) preparation of amino-functionalized silica through grafting of (3-aminopropyl)trimethoxysilane (APTMS). The textural data confirmed the uniform covering of the silica surface with the APTMS. At the same time, the irregular filling of silica pores was observed in the case of cobalt oxide-coated silica.

Cobalt imidazolate framework was synthesized according to the reported procedure [3]. The BET surface area of the obtained sample was 504 m²/g. The pore size distribution curve had two maximums corresponding to two types of pores (1.1 and 2.2 nm in diameter). Deposition of Co-MOF on modified silica surface was carried out under the same solvothermal conditions in the presence of the corresponding silica samples. Successful formation of Co-MOF phase on the amino-modified silica was confirmed by low-temperature N₂ adsorption study, XRD data and FT-IR spectroscopy, while Co-MOF did not grow up on cobalt oxide-coated silica surface. In the last case, a homogeneous nucleation of MOF predominated.

The NHPI was immobilized into pores of Co-MOFs/APTMS-SiO₂ by impregnation procedure from the solution. The selective localization of NHPI inside the pores of the MOF was confirmed by the significant decreasing of micropore volume of the obtained hybrid material in comparison with Co-MOFs/APTMS-SiO₂. The FT-IR spectrum of NHPI@Co-MOFs/APTMS-SiO₂ revealed the characteristic bands of all components of the hybrid material. The catalytic activity were tested in selective oxidation of cyclohexane.

References

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