Poster Presentation

MM-MOFs as catalysts for liquid-phase oxidation of toluene and cycloalkane

Abdul Malik Puthan Peedikakkal¹

¹Chemistry Department, King Fahd University Of Petroleum And Minerals, Dhahran, Saudi Arabia

E-mail: abdulmalik@kfupm.edu.sa

Selective oxidation of hydrocarbons is one of the most important class of chemical transformations in organic synthesis. Among these processes, toluene oxidation is an important transformation in chemical industry due to the vast applications of benzaldehyde, benzyl alcohol, benzoic acid and other oxygenated products that can be obtained [3]. Benzaldehyde is more valuable industrial product than benzoic acid due to its wide applications in the manufacture of pharmaceuticals, perfumes, polyurethane foams, and dyes. Currently, benzaldehyde is commercially produced via a benzyl chloride route which involves the chlorination of toluene followed by hydrolysis. This process, however, has a huge drawback as it generates large quantities of acidic/basic obnoxious waste solutions, leading to environmental pollution and equipment corrosion. Even worse, benzaldehyde produced via this route cannot be used to synthesize certain high-guality compounds like pharmaceuticals or perfumes because it inevitably contains significant amounts of chlorine. Also, direct hydroxylation of hydrocarbons has been identified as an intriguing class of oxidative reaction of toluene because of the low reactivity of aromatic C-H bonds and the low product selectivity. Consequently, several attempts have been made to develop new routes for the selective oxidation of toluene. Liquid-phase oxidation is industrially most preferred route due to the high selectivity of the catalytic reaction. Alkanes are naturally abundant and cheap carbon-containing raw materials, which serve as attractive substrates for the production of value-added organic chemicals. Unfortunately, the chemical inertness of these compounds is the main limitation towards their vast application for direct syntheses of oxygenated products under relatively mild conditions. Selective oxidation of saturated hydrocarbons is one of the major challenges in catalysis, especially conversion of cyclohexane into cyclohexanone and cyclohexanol. In recent times, metal-organic frameworks (MOFs) have generated significant attention as a revolutionary class of materials with a broad spectrum of applications ranging from carbon capture, gas storage, electronics, catalysis, and separation. These unique properties of MOFs as well as their welldefined crystal framework provide great opportunities to create specific desirable active sites and makes MOFs excellent candidates for catalytic applications. Currently, the investigations mainly explore the single-metal MOFs catalysts while the catalytic potentials of mixed-metal MOFs (MM-MOFs) species have not been well determined. The development of MM-MOFs catalysts is of unique interest because the incorporation of two or more kinds of metal atoms can significantly improve the activity and the selectivity of MOFs catalysts thereby creating a new class of active robust catalytic materials for more complicated catalysis such as multiple catalysis or cooperative catalysis. Herein, we report synthesis of MM-MOFs denoted as M-Zn-BTC, where M = Cu(II), Co(II), and Fe(II) using post-synthetic exchange (PSE) method. Catalytic performance of these materials was investigated in the oxidation of toluene, cyclohexane and methylcyclohexane in the presence of H2O2 as an oxidant and using acetonitrile as the solvent. Fe-Zn-BTC showed the best activity in terms of benzaldehyde selectivity for the oxidation of toluene. However, Cu-BTC gave the highest conversion for cyclohexane and methylcyclohexan

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