University of Zabol
Graduate school
Faculty of science
Department of Chemistry

Dissertation for Master's Degree in Organic Chemistry

Title:

Metal–organic frameworks and their hybridization with ionic liquids as new generation of catalysts in multi–component and oxidation reactions

Supervisors:
Dr. Esmael Sanchooli
Dr. Ali Reza Oveisi

Advisor:
Dr. Saba Daliran

By:
Mohadese Akbarian Moghaddam

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Abstract

A new Zr-basedMOF, namely, UiO-66-Urea, was prepared through polymerization between the 2-aminoterephthalate linkers of UiO-66-NH_2 MOF and 1,4-phenylene diisocyanate under mild reaction conditions. Post-synthetic coating of UiO-66-Urea with choline chloride (ChCl), as easily available, inexpensive, and nontoxic reagent, under thermal and solvent-free conditions resulted in *in-situ* formation of a deep-eutectic solvent-like on the UiO-66-Urea's surface, called here ChCl@UiO-66-Urea. The presence of $Zr_6O_4(OH)_4$ nodes and urea groups may capable of strong hydrogen bond formation with ChCl. The porous and bioinspired ChCl@UiO-66-Urea was characterized using FT-IR, powder XRD, SEM, EDX elemental mapping, TGA, and BET surface area measurements. Choline chloride-coated UiO-66-Urea was successfully promoted one-pot three-component synthesis of 2-amino-4H-chromenes, as biologically active heterocycles, through reactions of aldehydes, malononitrile, and α-naphthol or 4-hydroxycoumarin under solvent-free conditions. The catalytic activity of the respective solid was superior than UiO-66, UiO-66-NH_2, UiO-66-Urea, and even ChCl-2Urea due to synergistic effect between actives sites of UiO-66-Urea and ChCl. The reaction includes a consecutive three-step Knoevenagel condensation/Michael addition/cyclization mechanism.

In the second work, an iron-based metal-organic framework was prepared under solvothermal conditions and used as a heterogeneous catalyst for the aerobic oxidation of benzyl alcohols to benzaldehydes without any additives. The catalyst was characterized using FT-IR, PXRD, SEM, EDX. The catalyst can be reused up to 3 times in the reaction.

Keywords: Metal-organic frameworks, Zirconium-based MOF, Ionic liquid incorporation in MOF, Deep-eutectic solvent, 2-amino-4H-chromenes, Hybridization, Multi-component reactions (MCR), Fe-MOF, Heterogeneous catalysts, oxidative reactions.