THESIS INFORMATION

Title: METAL-ORGANIC FRAMEWORKS IRMOF-8, ZIF-9, MOF-199 AND IRMOF-3 AS CATALYSTS FOR THE FRIEDEL–CRAFTS ACYLATION, KNOEVENAGEL, AZA-MICHAEL AND PAAL-KNORR REACTIONS

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Abstract:

Highly porous metal-organic framework such as IRMOF-8, ZIF-9, MOF-199 and IRMOF-3 were synthesized by a solvothermal method, and used as an efficient heterogeneous catalyst for the Friedel-Crafts acylation reaction, Knoevenagel reaction, Aza Micheal reaction and Pal Knorr reaction. The solid catalyst was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. High conversions were achieved in the presence of a catalytic amount of the MOFs without the need for an inert atmosphere. The solid catalyst could be facilely separated from the reaction mixture by simple centrifugation, and could be reused without a significant degradation in catalytic activity. No contribution from homogeneous catalysis of active acid species leaching into the reaction solution was detected.

Main results:

Four different MOF materials such as IRMOF-8, ZIF-9, MOF-199, IRMOF-3 are synthesized by solvothermal methods in the existent laboratory conditions. The four MOFs were characterized by XRD, SEM, TEM to confirm their crystalline and porous

structure. Surface areas, determined by nitrogen adsorption/desorption isotherm are 2110 m^2/g for IRMOF-8, 1144 m^2/g for ZIF-9, 1970 m^2/g for MOF-199, 3295 m^2/g for IRMOF-3, which are compatible with other international researchers' results**.** Metal concentration in the solid MOFs was determined by AAS techniques, and their functional groups were characterized by FT-IR spectrometer.

The four MOFs were applied as catalysts in the four organic reactions: IRMOF-8 for Friedel- Craft acylation of of toluene with benzoyl chloride, ZIF-9 for Knoevenagel reaction between benzaldehyde and malononitrile, MOF-199 for aza-Michael reaction of benzylamine with ethyl acrylate and IRMOF-3 for the Paal-Knorr reaction of benzyl amine with 2,5-hexanedione, respectively.

Catalytic properties of the four MOFs were good as compared to other solid catalysts. The most important experiment was to investigate the leaching of active site of the solid catalysts into the reaction solution. Experimental results show that there was no any leaching or homogenous catalytic occurred in the four examined reaction. Lastly, the feasibility for the catalyst recyclability was tested and results show that the four catalysts were able to be reused up to five times without any significant degradation.

Based on the results obtained in this study, it can be concluded that MOF materials can be applied as catalysts in various reactions with advantages such as high efficiency, environment-friendly, and recyclability.

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