VIETNAM NATIONAL UNIVERSITY-HCMC

BACH KHOA UNIVERSITY

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THESIS INFORMATION

- Title: Application of Cu-MOF-74, $Cu_2(OBA)_2(BPY)$, MOF-235 as catalysts for carbon–heteroatom bond forming reactions
- Major: Chemical Engineering
- Major code: 62520301
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CONTENT

The objectives of thesis

Metal–organic frameworks (MOFs) have recently emerged as versatile materials in the field of heterogeneous catalysis due to their high surface area, modular nature and high crystallinity. Therefore, this thesis focuses on the investigation of the catalytic activities of Cu-MOF-74, $Cu_2(OBA)_2(BPY)$ and MOF-235 for the synthesis of benzazole, quinazoline, 4*H*-3,1-benzoxazine, aryl ether derivatives. These biologically active compounds are worthy of attention due to their numerous applications in pharmaceuticals and agricultural chemicals. However, it can be seen that MOF-catalyzed reactions for the synthesis of these compounds are quite limited.

Contribution of this thesis

These MOF-catalyzed reactions were not previously reported in the literature: (i) MOF-235 was utilized as a productive heterogeneous catalyst for the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles via one-pot oxidative cyclization reactions between 2-aminophenols or 2-aminothiophenols and alcohols (ii) The preparation of

4*H*-3,1-benzoxazines, quinazolines was performed via a one-pot, two-step process. The initial condensation of 2-aminobenzylamines/2-aminobenzyl alcohols with aldehydes, followed by oxidation of C–N bonds in the presence of $Cu_2(OBA)_2(BPY)$, TEMPO yielded the target product. (iii) Cu-MOF-74 was employed as a heterogeneous catalyst for the direct alkoxylation/ phenoxylation reaction of *N*-(quinolin-8-yl)benzamide with alcohols/phenols.

- In order for these reactions to be more widely used, the reaction scope with respect to each of coupling partners was considerably explored.
- These Cu-MOFs, Fe-MOF could be recovered and reutilized under these reaction conditions at least 5 times without significant decrease in catalytic efficiency. The crystallinity of used catalysts, as shown by P-XRD patterns, was almost intact as compared to that of fresh catalysts.

The most remarkable points

+ $Cu_2(OBA)_2(BPY)$ was used as solid catalyst for the mild synthesis of 4*H*-3,1-benzoxazines, quinazolines. The reaction had a broad scope, high tolerance of functional groups. In this reaction condition, combining of such a recyclable, solid catalyst and bio-related solvent for the synthesis of *N,N-; N,O*-heterocycles was not previously reported.

+ Cu-MOF-74 was found as catalyst in many C–N and C–O bond forming reactions. However, cross dehydrogenative coupling of alcohols/phenols with arenes to form C–O bonds catalyzed by a heterogeneous catalyst was not previously demonstrated. By using Csp^2–H alkoxylation methodology and heterogeneous catalysts, a new way to synthesize ethenzamide, an anti-inflammatory drug, or 2-(2-hydroxyethoxy)benzoic acid, an insulin inhibitor, was also reported. It is a highly efficient protocol since avoiding the contaminated metals from final products is highly demanding, especially in pharmaceutical industry.

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