Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

http://chemeng.hust.edu.vn/jca/

Cu-MOF-74 as a recycable catalyst for o-acetyl subsituted phenol ester synthesis via direct oxidative esterification of 2-(benzo[d]thiazol-2-yl)phenol with benzyl alcohol

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ARTICLE INFO

Received:
Accepted:

Keywords:
Cu-MOF-74,
benzyl alcohol,
benzoate,
2-(benzo[d]thiazol-2-yl)phenol,
ester.

ABSTRACT

A crystalline porous metal-organic framework Cu-MOF-74 (also known as Cu-CPO-27) was synthesized and characterized by several methods including PXRD, TGA, FT-IR, SEM, and nitrogen physisorption measurements. The Cu-MOF-74 was used as an efficient heterogeneous catalyst for the oxidative esterification of 2-(benzo[d]thiazol-2-yl)phenol with benzyl alcohol to form 2-(benzo[d]thiazol-2-yl)phenyl benzoate as desired product. The direct C–O coupling reaction could proceed readily, with more than 77 % reaction yield being achieved after 120 min at 100 °C in the presence of 5 mol% Cu-MOF-74 catalyst and *tert*-butyl hydroperoxide in decane as an oxidant. The Cu-MOF-74 exhibited higher activity than other MOFs and traditional homogeneous catalysts in the direct oxidative reaction. The Cu-MOF-74 could be recovered and reused three times without a significant degradation in catalytic activity and selectivity. To the best of our knowledge, this transformation using heterogeneous catalyst was not previously mentioned in the literature.

Introduction

Esterification is one of the important chemical reactions that have been used in a wide range of chemical industry [1]. Besides, the vast majority of esters have played a significant role in daily living that can be prepared by esterification reaction [2-3]. From this transformation, there are many methods to produce esters have been developed. Traditionally, the reaction between phenols and carboxylic acid derivatives could form phenol esters as main products in the presence of bases [4-6]. However, this method exhibited many disadvantages because it required a stoichiometric amount of bases, several steps along with the production of undesired side products [4-6]. To overcome these problems, the direct oxidative esterification could be studied. For example, by using Pd(OAc)2 as catalyst, Cheng and co-workers reported that phenol esters could be achieved from the esterification reaction of aldehydes with arylboronic acids under air condition [7]. Similarly, Lu et al demonstrated that the decarboxylation reaction between isatoic anhydrides and arylboric acids under an oxygen atmosphere could form phenol esters by using $Pd_2(dba)_3$ as catalyst [8]. Recently, based on transition-metal-catalyzed reaction, Yong et al mentioned using Cu(OAc)2 as a cheap catalyst to get phenol esters from the reaction of phenols with aldehydes utilizing organic oxidants [9]. In the presence of Cu(OAc)2 catalyst and *tert*-butyl hydroperoxide as a good oxidant, Sharma and his workers also synthesized phenol esters from the esterification of benzylic alcohols with 2-carbonyl substituted phenols [10]. With the current demand for environmentally benign