



Continuous synthesis of bis(indolyl)phenylmethane over acid modified H β zeolite

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ABSTRACT

The continuous synthesis of bis(indolyl)phenylmethane has been successfully accomplished for the first time by Friedel-Crafts alkylation of indole with benzaldehyde in a fixed-bed reactor over different zeolites. A citric acid modified H β (CA-H β) zeolite showed better catalytic performance than parent H β zeolite due to its larger surface area and smaller amount of weak acid sites, confirmed by the Brunauer-Emmett-Teller (BET) method, NH $_3$ temperature-programmed desorption (NH $_3$ -TPD) and Fourier Transform Infrared Spectrometer after adsorption of pyridine (Py-IR). Furthermore, it is proposed that citric acid treatment is appropriate for dealumination of H β zeolite, which results in the CA-H β zeolite having a larger number of active centers for the desired transformation. Significantly, CA-H β has shown good stability during a 100 h test.

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1. Introduction

Bis(indolyl)phenylmethane, a representative of the bis(indolyl)methanes, has attracted much interest in recent years due to its novel structure and important biological activities in the field of anticancer drugs [1]. Friedel-Crafts alkylation of indole with benzaldehyde is by far the most popular method for the synthesis of bis(indolyl)phenylmethane. Over a past few years, a series of catalyst systems have been reported, such as PEG-SO $_3$ H [2], pentafluorophenylammonium triflate [3], sodium lauryl ether sulfate [4], RuCl $_3$ ·3H $_2$ O [5], Schiff base-Cu(II) complex [6], sodium p-toluene sulfonate [7], LiClO $_4$ [8], NaHSO $_4$ ·SiO $_2$ [9], montmorillonite K10 clay [10], ZrOCl $_2$ ·8H $_2$ O/silica gel [11], AlPW $_{12}$ O $_{40}$ [12], Cu $_{1.5}$ PMo $_{12}$ O $_{40}$ [13], SBA-15-supported poly-(4-styrenesulfonyl(perfluorobutylsulfonyl)imide) [14], and Amberlyst-15 [9,15]. Although these catalysts are promising, many of these methods still suffer from one or more disadvantages like use of expensive reagents, excess of catalysts, extended reaction times, and complicated manipulations along with involvement of environmentally toxic media. Hence, there is still a need for an efficient, ecofriendly and cheap catalyst for the synthesis of bis(indolyl)phenylmethane and its analogs. Zeolites are regarded as a good choice due to their pore structures

and unique acid properties and have been investigated in this reaction [16–18]. For example, HY zeolite catalysts were used for the synthesis of this target using standard glassware by Reddy et al., showing good activity and reusability [16]. Karthik et al. found Zn $^{2+}$ ion-exchanged Y zeolite showed better activity than parent Y zeolite for the synthesis of bis(indolyl)phenylmethane owing to its higher Lewis acidity [17]. However, the reported methods were all batch process and lack of efficiency, therefore, it is desirable to develop a novel method for the effective synthesis of bis(indolyl)phenylmethane over zeolites.

Considering the benefit of continuous methods, they have been widely used not only in the laboratory but also on large-scale productions [19,20]. Friedel-Crafts reactions have been carried out continuously over solid acid catalysts in fixed-bed reactors due to the high efficiency [21–23]. For instance, Zhao et al. have reported that the Friedel-Crafts acetylation of anisole can proceed effectively over H β zeolites in a fixed-bed reactor, but their catalyst deactivated partly within 10 h [23]. On the other hand, the addition of acids has been proven to be important for improving the activity of zeolites [23–27]. For example, Srivastava et al. have reported that tartaric acid modified H β zeolite was an efficient catalyst for acylation and esterification reactions of aromatic compounds [26]. Recently, we have also investigated the influences of acids on the activity of H β zeolite in the Friedel-Crafts hydroxyalkylation of anisole with chloral. An oxalic acid modified H β (OA-H β) zeolite was found to have better catalytic performance than parent H β zeolite and partial regeneration of OA-H β zeolite can be achieved via subsequent calcination [27].

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