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Atom efficient Friedel–Crafts acylation of toluene with propionic anhydride over solid mesoporous superacid UDCaT-5

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ABSTRACT

Friedel–Crafts acylation is ubiquitous in industry and is typically carried out by using more than stoichiometric quantities of homogeneous catalysts. This creates pollution. In this work, acylation of toluene was studied in liquid phase with propionic anhydride with a variety of solid superacids to produce 4′-methylpropiophenone (4′-MPP). The solid superacids were modified versions of zirconia, namely, UDCaT-4, UDCaT-5 and UDCaT-6 developed in our laboratory; amongst which UDCaT-5 was the most active, selective and robust catalyst. The effects of various reaction parameters on the rate of reaction and selectivity were investigated to deduce the intrinsic kinetics of the reaction. The reaction is free from any external mass transfer as well as intraparticle diffusion limitations and is intrinsically kinetically controlled. The acylation conditions were: temperature 180 °C, toluene to propionic anhydride molar ratio 5:1, catalyst loading 0.06 g cm^{-3}, speed of agitation 1000 rpm, under autogenous pressure in a stainless steel autoclave reactor. Propionic acid generated *in situ* also reacts sequentially with toluene to give 4′-MPP. A conversion of 62% of priopionic anyhydride is obtained after 3 h, with 100% mono-acylated product containing 67% 4′-MPP. Water is the only co-product of the overall reaction. A suitable kinetic model was developed. The reactions were carried out without using any solvent in order to make the process cleaner and greener.

1. Introduction

Liquid acids have been extensively used as catalysts in a variety of chemical and allied industries. Green chemistry approach involves the replacement of corrosive and toxic liquid acids such as HF and H_2SO_4 by environmentally benign heterogeneous solid acids. The production of various pharmaceuticals, agrochemicals, dyes and pesticides involves the synthesis of aromatic ketones and their derivatives. The common routes for preparation of these ketones proceed *via* Friedel–Crafts acylation of the concerned aromatic hydrocarbon with derivates of carboxylic acids, which are traditionally catalyzed by either Lewis acids such as $AlCl_3$, $FeCl_3$ and BF_3 or Brønsted acids such as HF or H_3PO_4 [1]. 4′-Methylpropiophenone (4′-MPP) is found to have wide applications in the area of fine chemicals, pharmaceuticals, resins, drugs, perfumes and specialty chemical synthesis. The classical production of 4′-MPP is performed by Friedel–Crafts acylation process of toluene with propionic anhydride or propionyl chloride, using stoichiometric quantities of conventional homogeneous Lewis acid catalyst, $AlCl_3$, $FeCl_3$ or BF_3 [2]. Use of these catalysts is fraught with a numerous drawbacks and operational problems. More than stoichiometric amount of Lewis acid is required. The reaction complexes formed are rather stable and their break-up to obtain the desired product leads to the loss of the catalyst [1,3]. The corrosive nature of homogeneous acids results in premature ageing of the processing equipment and associated transfer lines, which is expensive. Use of solid acids such as shape selective zeolites in acylation with carboxylic acids is more attractive [4].

In recent years, efforts have been directed toward the promotion of solid acid catalysts and several synthetic procedures have been reported. Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts [5–7]. They are non-corrosive; presenting fewer disposal problems, and their separation from fluid phase is much easier, which allows their repeated use. They permit the use of cheaper and non-polluting reagents, and offer several different reactor configurations [3]. In addition, physical and chemical properties of solid acids can be tailored and tuned to promote reactivity and selectivity and prolonged catalyst life [7]. Nakamura et al. [8] described the propionylation and butyrylation of toluene with propionic anhydrides and butyric anhydrides over SO_4/ZrO_2, SO_4/SnO_2, Pt-SO_4/ZrO_2, and Ru-SO_4/ZrO_2; yields of 7–9% *o*- and 91–93% *p*-isomers were 31, 26, 32, and 44% for propionylation and 46, 29, 44, and 55% for butyrylation, respectively obtained.

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