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Friedel–Crafts propionylation of veratrole to 3,4-dimethoxypropiophenone over superacidic UDCaT-5 catalyst

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ABSTRACT

3,4-Dimethoxypropiophenone (3,4-DMPP) is of considerable commercial importance due to its use in fine chemical and drug industries. 3,4-DMPP is traditionally produced by the Friedel–Crafts propionylation of veratrole using homogeneous catalysts which are highly polluting. Zeolites have also been used but they are known to deactivate rapidly. A variety of novel solid acid catalysts such as UDCaT-4 (persulfated alumina zirconia on hexagonal mesoporous silica, HMS), UDCaT-5 (superacidic modified sulfated zirconia) and UDCaT-6 (modified sulfated zirconia nanoparticles on HMS) were synthesized in our laboratory and characterized. Amongst them UDCaT-5 was the most active and selective. The current work deals with development of clean and benign route for 3,4-DMPP synthesis using UDCaT-5 as catalyst in the absence of any solvent. Effects of various parameters were studied in order to optimize the conversion of veratrole and selectivity to 3,4-DMPP. Based on the experimental data a suitable mathematical model was developed to represent the reaction kinetics.

1. Introduction

Friedel–Crafts acylation and alkylation reactions are amongst the most versatile methods of synthesizing substituted aromatic compounds which serve as precursors for a variety of industrial processes [1]. Aromatic ketones are valuable intermediates as well as end products in an extensive range of value-added chemicals, which include pharmaceuticals, agrochemicals, biocides, flavors, fragrances and fine chemicals [2].

3,4-Dimethoxypropiophenone (3,4-DMPP) is of considerable commercial importance due to its use in fine chemical and drug industries. 3,4-DMPP is traditionally produced by the Friedel–Crafts propionylation of veratrole (VT) by using homogeneous catalysts such as $AlCl_3$, $TiCl_4$, $FeCl_3$, $SnCl_4$, CF_3SO_3H, FSO_3H and H_2SO_4 [3,4]. These catalysts are highly polluting and corrosive. More than stoichiometric quantities of the catalyst are used which are neutralized at the end of reaction leading to effluent treatment problems. Recently, the use of solid catalysts, such as Nafion-H [5], clays [6], heteropoly acids [7], $FeSO_4$, $Fe_2(SO_4)_3$ and metal oxides promoted by sulfate ions (SO_4^{2-}/Al_2O_3), SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2), have been reported for the Friedel–Crafts of acylation of aromatics [7–9]. However, there is a limited literature on veratrole propionylation to 3,4-DMPP [10].

In particular, sulfated zirconia is the most powerful solid superacid which is used in a number of reactions of industrial utility [11–19]. All published literature shows that sulfated zirconia has been prepared with a maximum 4% w/w of sulfur with preservation of tetragonal phase which is responsible for its superacidic nature. Above this sulfur content, the tetragonal phase of zirconia is strongly affected and the superacidity reduced. It would be most advantageous to synthesize sulfated zirconia with sulfur content above 4% while retaining the tetragonal phase to attain high superacidity. A series of novel catalysts, named as UDCaTs, were thus prepared. These catalysts have been tested in a number of reactions in our laboratory [20–24]. Yadav and Murkute reported for the first time the preparation of sulfated zirconia with the highest sulfur content (9%), by using chlorosulfonic acid as a new source for sulfate ion [23]. This new catalyst was designated as UDCaT-5. The acronym, UDCaT stands for the University Department of Chemical Technology (UDCT) by which this institute was popularly known until recently.

The current work delineates novelties of UDCaT series of catalysts in Friedel–Crafts acylation of veratrole using propionic anhydride under solventless conditions. UDCaT-5 was found to be the most active, selective and robust catalyst. The overall process is green and clean. This work also deals with development of a kinetic model.

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