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Green route for the chlorination of nitrobenzene

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ABSTRACT

A new green chlorination process of deactivated aromatics has been developed, being environmental-friendly and allowing the continuous chlorination of 1.7 kg nitrobenzene/kg catalyst per day.

The triple novelty consists of using a non-conventional chlorination agent, the *trichloroisocyanuric acid* (TCCA, $C_3N_3O_3Cl_3$), along with solid acid catalysts (mainly zeolites) in a continuous flow reactor system. Different zeolites and solid acids have been tested in the chlorination of nitrobenzene, chosen as a model deactivated aromatic substrate.

HUSY zeolite was found as the more promising catalyst for performing the chlorination of nitrobenzene, with good conversions (39–64%) at high selectivity toward monochlorinated products (90–99%). Finally, it is worthy to note that HUSY zeolite could be reused for at least five successive runs.

1. Introduction

Chloroarenes are valuable starting molecules in fine chemistry, for the synthesis of dyes, bio-active compounds such as pesticides or pharmaceuticals [1,2]. Unfortunately, the conventional industrial methods used for the chlorination of aromatics usually produce mixtures of regioisomers, difficult to separate, thus raising the cost for the industry [3]. Indeed, the utilization of Cl_2, a toxic gas, as chlorine source produces a large quantity of non-recyclable wastes. Another disadvantage is the use of toxic acid catalysts such as Lewis acids (aluminum chloride or boron trifluoride), which are consumed and need to be neutralized after the reaction. In parallel, strong Brønsted acid catalysts such as H_2SO_4 remain very corrosive and generate a lot of salts as co-products.

During the past decades, researchers focused on the development of more efficient and selective processes for the chlorination of arenes [4–7]. For instance, Esteves et al. [7a] developed a methodology for the chlorination of deactivated arenes using trichloroisocyanuric acid (*TCCA*, $C_3N_3O_3Cl_3$) in a superelectrophilic medium.

TCCA is a stable and inexpensive solid, easily available in pool supplies, being thus frequently used as swimming-pool disinfectant and bleaching agent. It is an efficient chlorine source due to its high chlorine content, which can be up to 45.5% in weight, allowing *a priori* a higher atomic efficiency than its N-chloro analogs [7b]. TCCA was successfully used for chlorination of electron-rich arenes [7b], alkenes [8] and carbonyl compounds [9], preparation of N-chloro substrates [10,11] and in diverse oxidation reactions [12].

Nowadays, organic chemistry is increasingly moving toward green chemistry, where both homogeneous and heterogeneous catalysis are at the core of this concept. In heterogeneously catalyzed reactions, zeolites represent the key solid acid materials in petrochemistry [13,14]. In addition, thanks to their internal porosity, zeolites provide a highly organized channel structure and strong acidity. The combination of these properties led them to exhibit high conversions and excellent selectivities in targeted reactions [15,16].

The chlorination of nitrobenzene is a very important process for the production of series of useful compounds in dye chemistry [17]. It is worthy to study the chlorination of nitrobenzene in order to produce valuable intermediates for the synthesis of azo dyes.

The aim of the present study is therefore to develop a new chlorination process of deactivated aromatics, being more environmental-friendly by the use of solid acids instead of liquid acids. In order to achieve this goal, we set up both a catalytic and a

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