



5th National Conference on New Researches in Chemistry and Chemical Engineering Tehran-2019

A Review of Heterogeneous Catalysis Esterification

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ABSTRACT

The conventional way to produce esters is the esterification of carboxylic acids with alcohols catalyzed by homogeneous catalysts such as sulphuric acid. These homogeneous catalyst reactions suffer from several drawbacks, such as the difficulties of catalyst separation from the reaction mixture, formation of side reactions and the corrosion of reactors.

Therefore the attention of many research studies has turned to the replacement of homogeneous catalysts with heterogeneous catalysts. In this paper detailed application of heterogeneous esterification over heteropolyacids (HPAs), ion-exchange resins as well as zeolites are described.

Keywords: esters, homogeneous, homogeneous catalyst, heterogeneous, heteropolyacids, ion-exchange resins, zeolites

1. AN INTRODUCTION TO ESTERS

In chemistry esters are compounds derived from carboxylic acids, usually in reactions with alcohols along with the elimination of water [1]. Esters are also formed by a number of other reactions utilizing acid anhydrides, acid chlorides, amides, nitriles, unsaturated hydrocarbons, ethers, aldehydes, ketones, alcohols, and esters (via ester interchange). Esters usually have a sweet smell and are considered high-quality solvents for a broad array of plastics, plasticizers, resins, and lacquers [2] to [3].

In addition, homogeneous catalysts generate huge amount of wastewater, and can be corrosive that lead to corrosion on reactor and pipelines besides being energy intensive and high cost. Heterogeneous catalysts are much preferred catalysts since the reaction can occur under mild reaction condition. They are less energy intensive, easily separated from product, and exhibit high possibility to regenerate and reuse.

1.1 Reactions between organic acids and alcohols

When a carboxylic acid is treated with an alcohol and an acid catalyst, an ester is formed (along with water). This reaction is called the Fischer esterification. [4] Fischer esterification or Fischer-Speier esterification is a special type of esterification by refluxing a carboxylic acid and an alcohol in the presence of an acid catalyst. The reaction was first described by Emil Fischer and Arthur Speier in 1895. Most carboxylic acids are suitable for the reaction, but the alcohol should generally be a primary or secondary alkyl. Tertiary alcohols are prone to elimination. Commonly used catalysts for a Fischer esterification include sulfuric acid, tosylic acid, and Lewis acids such as scandium (III) triflate. For more valuable or sensitive substrates (for example, biomaterials), dicyclohexylcarbodiimide is often used. The reaction is often carried out without a solvent (particularly when a large reagent excess of alcohol is used) or in a non-polar solvent (e.g. toluene) to facilitate the Dean-Stark method. Typical reaction times vary from 1–10 hours at temperatures of 60–110 °C. [5] to [6]

1.1.1 Esterification of ethyl acetate

Direct acylations of alcohols with carboxylic acids is preferred over acylations with anhydrides (poor atom economy) or acid chlorides (moisture sensitive). The main disadvantage of direct acylation is the unfavorable chemical equilibrium that must be remedied (e.g. by a large excess of one of the reagents), or by the removal of water (e.g. by using Dean-Stark distillation, anhydrous salts, molecular sieves, or by using a stoichiometric quantity of acid catalyst). [7]