

Fluorous Lewis Acid-Catalyzed Reactions Development

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Received: October 05, 2021; Accepted: October 17, 2021; Published: October 23, 2021

Abstract

Organic synthetic technique in the twenty-first century strives to follow the principles of Green Sustainable Chemistry (GSC), and we may predict that GSC will become a major goal for chemical enterprises in the future. Synthetic organic chemistry's main goal is to develop waste-free and environmentally friendly industrial processes using Lewis acids like aluminium chloride. The development of a "catalyst recycling system that harnesses the high activity and structural properties of fluorous Lewis acid catalysts" has been a fundamental technological goal of our work in this field. As a result, we've produced a range of new fluorous Lewis acid catalysts, including bis (perfluoroalkanesulfonyl) amides or tris (perfluoroalkanesulfonyl) methides of ytterbium (III), scandium (III), tin(IV), or hafnium(IV). In a Fluorous Biphasic System (FBS), in supercritical carbon dioxide, and on fluorous silica gel supports, our catalysts are recyclable and effective for acylations of alcohols and aromatics, Baeyer-Villiger reactions, direct esterifications, and transesterifications.

Keywords: Fluorous chemistry; Lewis acid; Sulfonimide; Biphasic system; Aqueous reaction

Introduction

Lewis acid-mediated reactions involving aluminium chloride generally produce a lot of acidic waste in addition to the desired product (s). With this in mind, we set out to create new reaction processes catalysed by highly active, selective, and recyclable Lewis acids that would considerably minimise acidic wastes and might potentially replace existing aluminium chloride methods. A series of fluorous biphasic reactions catalysed by fluorous Lewis acids with a large number of fluorine atoms, heterogeneous Lewis acid-catalyzed reactions using fluorous silica gel-supported fluorous Lewis acids, and fluorous Lewis acid-catalyzed reactions in supercritical carbon dioxide are described here. In carbon-carbon bond producing processes like the Diels-Alder reaction, Mukaiyama aldol reaction, and Friedel-Crafts acylations, fluorous Lewis acid catalysts were found to be both helpful and recyclable [1]. Friedel-Crafts acylation of anisole and related aromatic compounds, in particular, requires an equimolar or greater amount of a catalyst, such as aluminium chloride, whereas Friedel-Crafts acylation of anisole and related aromatic compounds went well. Because this catalyst was also recyclable, it was a win-win situation. As both nucleophilic aromatics and solvents, toluene and even chlorobenzene could be employed. Due to their very water-repellent qualities, fluorous Lewis acid catalysts, which catalyse many processes at the organic/fluorous interface, are water stable. As a result, it was thought that fluorous Lewis acid catalysts may be utilised in water-based reaction systems. The direct esterification processes utilising $\text{Hf}[\text{N}(\text{SO}_2\text{-n-C}_8\text{F}_{17})_2]_4$ as a catalyst were investigated. The catalytic reactions of an equimolar quantity of carboxylic acid and alcohol were carried out at a low temperature (less than 100°C) without distilling the water produced as a by-product. As expected, the hafnium (IV) catalyst was recyclable. Because water is immiscible in both the organic and fluorous phases, it was assumed that water rapidly flowed out of the reactive site at the organic/fluorous interface. The Baeyer-Villiger reaction is a useful process for converting ketones into esters or lactones. Ketones are often treated with a stoichiometric dose of a potentially explosive concentrated organic peracid such as peracetic acid or perbenzoic acid to carry out this reaction [2]. Utilizing our fluorous catalysts, we devised an environmentally friendly Baeyer-Villiger oxidation using commercially available and less explosive 35 percent aqueous hydrogen peroxide solution. $\text{Sn}[\text{N}(\text{SO}_2\text{-n-C}_8\text{F}_{17})_2]_4$ was discovered to be the most effective catalyst for lactonization of cyclic ketones such as 2-adamantanone after

testing other catalysts. Fluorous solvents have a higher density than conventional organic solvents. We constructed an unique continuous-flow reaction apparatus based on this principle, which comprised of a reactor with a mechanical stirrer and a decanter. The fluorous solvent is put into the reactor, then a fluorous catalyst such as $\text{Yb}[\text{N}(\text{SO}_2\text{-C}_{10}\text{HF}_{20}\text{O}_3)_2]_3$ is added, which is immobilised in the fluorous solution due to its insolubility non normal organic solvents. The mobile organic phase, which contains organic substrates and reagents, continuously flows into the reactor and is violently agitated with the stationary fluorous phase. The emulsion mixture is automatically fed to the decanter after the reaction, where the organic and fluorous phases are separated. The upper organic phase, which contains the product(s), overflows and is collected, while the lower fluorous phase is recycled, allowing the substrates to be easily converted to products in this continuous-flow system. The application of this method to industrial operations is critical [3].

Conclusion

In a fluorous biphasic system, immobilised on fluorous silica gel, and in supercritical carbon dioxide, we established a number of useful reactions catalysed by novel fluorous Lewis acids $\text{M}(\text{N}(\text{SO}_2\text{-n-C}_8\text{F}_{17})_2)_n$. In many situations, the catalysts were recyclable, allowing for the decrease of acidic waste. For industrial applications, we developed a continuous-flow reaction system based on the fluorous biphasic system. Fluorous catalytic reaction methods can be used to synthesise a variety of products, including fine chemicals, pharmaceutical and pesticide intermediates, and are projected to become a viable technology for reducing acidic wastes in the near future.

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