Polymer-Supported Rare Earth Catalysts Used in Organic Synthesis

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Abstract. Three types of polymer-supported rare earth catalysts, Nafion-based rare earth catalysts, polyacrylonitrile-based rare earth catalysts, and microencapsulated Lewis acids, are discussed. Use of polymer-supported catalysts offers several advantages in preparative procedures such as simplification of product work-up, separation, and isolation, as well as the reuse of the catalyst including flow reaction systems leading to economical automation processes. Although the use of immobilized homogeneous catalysts is of continuing interest, few successful examples are known for polymer-supported Lewis acids. The unique characteristics of rare earth Lewis acids have been utilized, and efficient polymer-supported Lewis acids, which combine the advantages of immobilized catalysis and Lewis acid-mediated reactions, have been developed.

Keywords: Lewis acids, Polymer-supported catalysts, Rare earth triflate, Combinatorial synthesis, Carbon–carbon bond-forming reactions

1 Introduction

Use of polymer-supported catalysts offers several advantages in preparative procedures. Simplification of product work-up, separation, and isolation as well as reuse of the catalyst including use of flow reaction systems could lead to economical automation processes. Although the use of immobilized homogeneous catalysts is of continuing interest [1], few successful examples are known for polymer-supported Lewis acids [2,3]. This is probably due to the instability of most Lewis acids to air (moisture) and water. During preparation of polymer-supported catalysts, many manipulations have to be carried out in air or in the presence of water. On the other hand, it was recently found that some rare earth Lewis acids are stable in water [4]. Utilizing this very unique characteristic, several efforts to develop efficient polymer-supported Lewis acids combining the advantages of immobilized catalysis and Lewis acid-mediated reactions, have
been made. In this chapter, three types of polymer-supported rare earth catalysts, Nafion-based rare earth catalysts, polyacrylonitrile-based rare earth catalysts, and microencapsulated Lewis acids are discussed [5].

2 Nafion-Based Rare Earth Catalysts

Recently, scandium triflate \([\text{Sc(OTf)}_3]\) was found to be stable in water and successful Lewis acid catalysis was carried out in both water and organic solvents [6–8]. \(\text{Sc(OTf)}_3\) coordinates to Lewis bases under equilibrium conditions, and thus activation of carbonyl compounds using a catalytic amount of the acid has been achieved [6,7]. In addition, effective activation of nitrogen-containing compounds such as imines, amino aldehydes, etc. has been performed successfully [8]. Encouraged by the characteristics and the usefulness of \(\text{Sc(OTf)}_3\) as a Lewis acid catalyst, a polymer-supported scandium catalyst was prepared.

Nafion (NR-50, Du Pont) was chosen as the supporting framework [9]. Three equivalents of Nafion were treated with \(\text{ScCl}_3\cdot 6\text{H}_2\text{O}\) in acetonitrile under reflux conditions [10]. After 40 h, 96% of the \(\text{ScCl}_3\cdot 6\text{H}_2\text{O}\) was consumed and the polymer thus prepared (Nafion-Sc) contained 1.3% Sc, according to ICP analysis. Choice of solvent is important at this stage; only 27% of the \(\text{ScCl}_3\cdot 6\text{H}_2\text{O}\) was consumed when 1,2-dichloroethane was used as the solvent. This Nafion-Sc catalyst was then tested in several synthetic reactions [11]. First, alkylation reactions of carbonyl compounds were investigated. Alkylation reactions of carbonyl compounds are among the most important carbon–carbon bond-forming reactions, and the products, homoallylic alcohols having hydroxyl and double bond groups, are synthetically useful intermediates [12]. Nafion-Sc was also found to be effective in the alkylation reactions of carbonyl compounds with tetraallylitan, and selected examples are shown in Table 1 [13]. In all cases, the reactions proceeded smoothly in both organic and aqueous solvents to afford the desired homoallylic alcohols in high yields. Not only aldehydes, but also ketones worked well. Moreover, use of aqueous solvents enabled the reactions of non-protected carbohydrates [14]. Non-protected sugars reacted directly with tetraallylitan to give the adducts, which are useful intermediates for the synthesis of higher sugars. Salicylaldehyde and 2-pyridinecarboxaldehyde reacted with tetraallylitan to afford the corresponding homoallylic alcohols in good yields. These compounds are known to react with the Lewis acids rather than the nucleophile under general Lewis acidic conditions.

Nafion-Sc was also found to be effective in some other reactions (Schemes 1–3). In typical Lewis acid-mediated reactions, such as Diels–Alder, Friedel–Crafts acylation, and imino Diels–Alder reactions, Nafion-Sc worked efficiently to afford the corresponding adducts in high yields.

It was also found that Nafion-Sc could be easily recovered and reused. The catalyst was recovered simply by filtration and washing with a suitable solvent, and the activity of the recovered Nafion-Sc was comparable to the fresh catalyst; in the reaction of benzaldehyde with tetraallylitan in \(\text{H}_2\text{O/MeOH/toluene}(1:7:4)\)