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Chitosan: a highly efficient renewable and recoverable bio-polymer catalyst for the expeditious synthesis of α-amino nitriles and imines under mild conditions†

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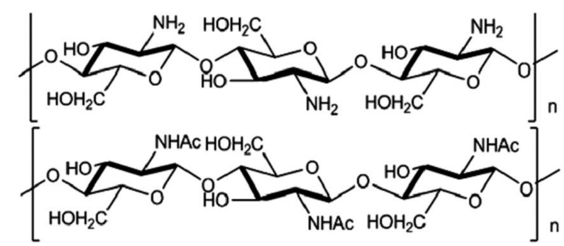
Commercial chitosan – without any post-modification with active Bronsted or Lewis acid centers – was found to be a highly efficient renewable and recoverable bio-polymer catalyst for the rapid and convenient synthesis of α-amino nitriles or imines from aromatic aldehydes and amines under mild reaction conditions at room temperature in high to quantitative yields. The α-amino nitrile derivatives were prepared through the Strecker reaction using trimethylsilyl cyanide (TMSCN) and catalyzed by chitosan as a heterogeneous bifunctional organocatalyst.

Introduction

In recent years, development of new processes that minimize pollution in chemical synthesis has received considerable attention due to growing environmental concerns. In this respect, heterogeneous catalysis has emerged as a useful tool to reduce waste production with regard to simplicity of the processes, lower contamination of the products with the active catalytic species, avoiding the use of toxic solvents, separation and recycling of the catalysts, and potential to apply continuous flow *versus* batch configuration on technical scales.[1,2] For this purpose, metallic species or other catalytic active centers have been often immobilized on inorganic materials such as SiO_2, Al_2O_3, ZrO_2, TiO_2 or MgF_2, synthetic organic polymers or their hybrid materials.[1–5] Further development of this strategy has resulted in exploring nano-ordered heterogeneous catalysts.[6–8] On the other hand, biopolymers such as starch,[9] cellulose,[10] chitosan[2] or wool[11] have been used as a support in heterogeneous catalytic systems very recently. However, extensive progress in designing more sustainable chemical processes takes place if biopolymers themselves without any post-modification can be used as heterogeneous catalysts. In this context, chitosan can play a major role as a natural, biodegradable, and biocompatible polymer. Literature survey shows that a wide range of applications have been reported for chitosan in different fields such as medicine, drug delivery, food packaging,

1a

1b



Scheme 1 Chemical structure of chitosan (**1a**) and chitin (**1b**).

cosmetics, water treatment, membranes, fuel cells, hydrogels, adhesives, and surface conditioners. Indeed, chitosan as a linear polyamine is the most important derivative of chitin, the second most abundant natural polymer in the world after celloluse. Chitin itself is a byproduct of the fishery industry (Scheme 1).[12]

The presence of free NH_2 groups in chitosan and its insolubility in most organic compounds and pure water explains the greater potential of chitosan than chitin for use in different areas of the chemical industry including heterogeneous catalysis. Since chitosan has both hydroxyl and amino groups, it can be modified chemically into many forms and can participate in different types of chemical reactions as a suitable support for different catalytic species.[2,13] Furthermore, the use of small natural or synthetic organic molecules, namely organocatalysis, has provided attractive alternatives to the more traditional metal-catalyzed variants and in many cases has obviated the need for prior activation of the reaction components in separate steps, especially for asymmetric transformations in recent years.[14] Hence, chitosan, as a natural poly-glucosamine, can be explored without any post-modification, as a mild bifunctional heterogeneous catalyst in organic synthesis. In this

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