

Application of natural catalysts in the synthesis of organic compounds

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Maryam Sadat Ghasemzadeh was born in Ghaen/ Southern Khorasan, Iran. She received her B.Sc. in Pure Chemistry from Imam Khomeini International University and M.Sc. in Organic Chemistry from Birjand University under the supervision of Professor Sara Sobhani. She is currently studying her Ph.D. in Ferdowsi University of Mashhad under the supervision of Professor Batool Akhlaghinia. Her current research focuses on new heterogeneous nanocatalysts to develop new methods of organic synthesis.

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

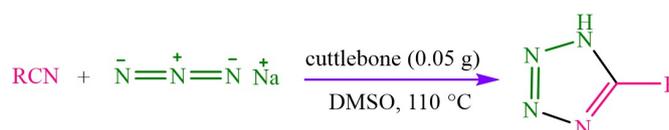
Introduction

Based on the principles of “green and sustainable chemistry”, one of the most interesting developments in the synthetic organic chemistry is applying the environmentally benign reagents and

reaction conditions. Nowadays, the development of eco-friendly, nontoxic, inexpensive and recyclable catalysts with improved efficiency has attracted a great deal of interest [1,2].

Abstracts

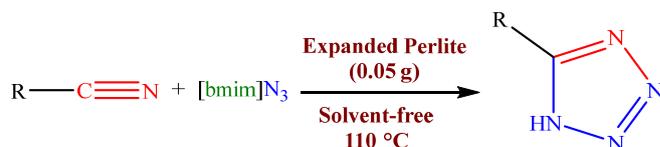
(A) Akhlaghinia *et al.* in 2015 reported synthesis of 5-substituted-1*H*-tetrazoles by [3+2] cycloaddition reaction of nitriles with sodium azide. The reaction was catalyzed by cuttlebone as a green heterogeneous catalyst with high porosity, flexural stiffness, compressive strength and thermal stability in DMSO at 110 °C. Additionally, Aryl, heteroaryl and alkyl nitriles, sterically hindered *ortho*-substituted aryl nitriles, organic nitriles containing bulky aryl groups and halo aryl nitriles used to produce 5-substituted-1*H*-tetrazoles [3].



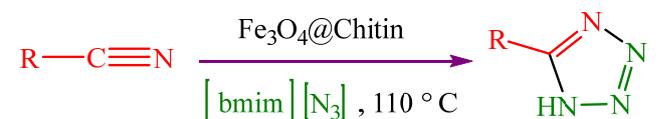
(B) Akhlaghinia *et al.* in 2015 described Ce (III) immobilized on an aminated epichlorohydrin-activated agarose matrix (CAEA) as a natural, effective and reusable heterogeneous catalyst for the transamidation of carboxamides with amines under solvent-free conditions. Furthermore, a wide range of aromatic and aliphatic amides were used to the synthesis of carboxamides. Additionally, easy work-up, simple separation, reusability and also high efficiency make this procedure a useful method for preparation of carboxamides [4].



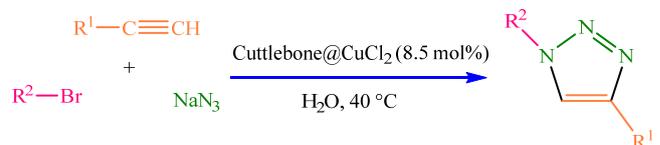
(C) Akhlaghinia *et al.* in 2015 reported expanded perlite as a natural heterogeneous catalyst for the one-pot synthesis of 5-substituted-1*H*-tetrazoles from nitriles and [bmim]N₃ in solvent-free conditions. This green catalyst has the advantages of stability, low-toxicity and recyclability. Moreover, insignificant loss in catalytic performance and product yield was observed even after six cycles [5].



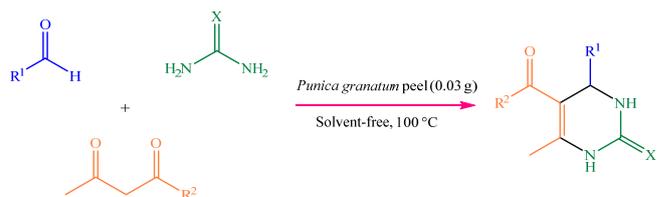
(D) An efficient, eco-friendly and simple method for the synthesis of 5-substituted-1*H*-tetrazoles catalyzed by magnetite-chitin (Fe₃O₄@chitin) as a green and recyclable catalyst was reported by Akhlaghinia *et al.* in 2016. This study described the synthesis of a variety of tetrazoles through the reaction of nitriles with 1-butyl-3-methylimidazolium azide ([bmim][N₃]) under solvent-free conditions. Minimization of chemical waste, easy preparation of the catalyst and its recyclability up to six runs and excellent yield of products in short reaction times were the important advantages of this method [6].



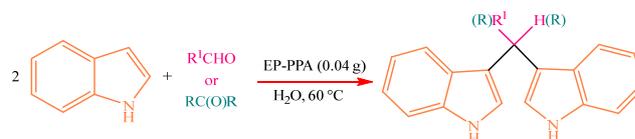
(E) In 2015, Akhlaghinia and co-workers reported Cuttlebone@CuCl₂ as a natural and efficient heterogeneous catalyst for the synthesis of 1,4-disubstituted 1,2,3-triazole derivatives in water. Besides, being ligand-free, leaching-free, thermally stable, environmentally friendly and recyclable for seven times were the advantages of this protocol [7].



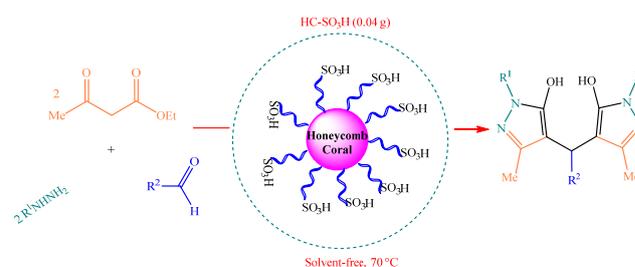
(F) In 2017, Akhlaghinia and co-workers reported Biginelli condensation reaction using punica granatum peel as an effective and inexpensive heterogeneous organocatalyst for producing 3,4-dihydropyrimidin-2(1*H*)-one/thiones derivatives in high to excellent yields. The punica granatum peel was reused and recovered seven times without significant decrease in its activity, which can be the most significant advantage of this method [8].



(G) The catalytic activity of the Expanded Perlite-Polyphosphoric acid (EP-PPA) was utilized as a new, effective, recyclable and eco-friendly heterogeneous catalyst for the synthesis of aryl/alkylbis(indolyl)methanes, in water. Additionally, shorter reaction times, cleaner reaction profiles and simple work-up procedures are some advantages of this protocol [9].



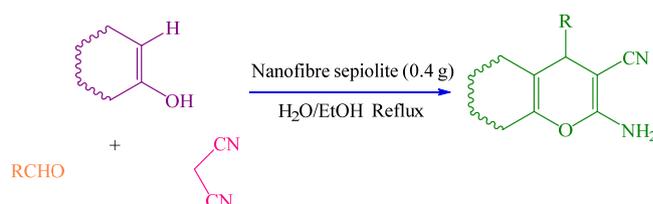
(H) In 2017, Akhlaghinia and co-workers introduced Sulfonated Honeycomb Coral (HC-SO₃H) as a novel, green and recoverable solid acid heterogeneous catalyst for the synthesis of 4,4'-(aryl methylene)bis(3-methyl-1*H*-pyrazol-5-ol)s. This approach has some advantages such as quick reaction times, non-toxicity of the catalyst and solvent-free conditions [10].



(I) The nano-structured solid catalyst (calcined oyster shell nanoparticles (COS NPs)) was reported by Akhlaghinia *et al.* in 2017 as an efficient and eco-friendly catalyst. COS NPs was used for the synthesis of 1,8-dioxo-octahydroxanthenes *via* the one-pot condensation reaction of 5,5-dimethyl cyclohexane-1,3-dione (dimedone) with various aldehydes under solvent-free conditions. This synthetic pathway is a green protocol offering important advantages, such as solvent-free reactions, reusability of the catalyst up to six runs, short reaction time and simple workup procedure [11].



(J) Nanofibre sepiolite has been also applied as a nanostructured and green catalyst for the rapid, clean, and highly efficient synthesis of 2-amino-4*H*-chromene derivatives. Aromatic aldehydes were reacted with various enolizable C-H bonds (such as dimedone, *a*-naphthol, resorcinol, and 4-hydroxy-2*H*-chromen-2-one), and malononitrile in a mixture of water/ethanol to produce desired products [12].



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