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Activated Fuller's earth as an inexpensive, eco-friendly, efficient catalyst for the synthesis of 5-aryl 1-*H*-tetrazole *via* [3+2] cycloaddition of nitriles and sodium azide

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ABSTRACT

A simple and efficient method for the preparation of 5-aryl 1-*H*-tetrazoles was developed from various aryl nitriles and sodium azide (NaN_3) *via* [3+2] cycloaddition reaction using activated Fuller's earth as an efficient heterogeneous catalyst. This catalyst has advantageous of cost, stability, recovery, reusability, and ecological benefits along with high product yield, and mild protocol.

Nowadays chemistry of heterocycles has acquired enormous importance.[1] Tetrazoles which belongs to the heterocyclic class has attracted considerable importance because of wide usefulness[2,3] and applications as heterocyclic ligands in coordination chemistry, material sciences, pharmaceuticals, explosives, photography[4–8] as well as plant growth regulators.[9] A well-known tetrazole, dimethyl thiazolyl diphenyl tetrazolium bromide (MTT) is used in the MTT cell proliferation assay.[10] Biphenyl tetrazoles are intermediates to synthesize sartan drugs (Fig. 1). Tetrazoles have been extensively used as a bioisostere of carboxylic acids in molecular design,[4] and also used in the preparation of imidoylazides.[11] Tetrazoles containing molecules possess various biological activities *viz.* antiulcer,[12] anticonvulsant,[13] antiviral, antibacterial, antifungal, anti-inflammatory,[14] antihistaminics,[15] and antitubercular.[16]

The usual method for preparation of tetrazole is through the addition of azide ion to organic nitrile.[17–21] Various methods have been reported for the preparation of 5-aryl 1-*H*-tetrazoles; however, most of the methods have certain boundaries with regard to scope and reaction conditions; e.g. cost of synthesis, harsher reaction conditions, longer reaction time, lower yields, and the use of expensive, explosive and toxic reagents.[22] In order to overcome these limitations, Sharpless and co-workers reported a relatively simple, convenient, and safe procedure for the synthesis of tetrazole by the addition of sodium azide to nitriles catalyzed by (50 mol%) Zn (II) salts.[23,24] In spite of the advantages of homogeneous catalysts, this procedure hinders its use in the industry due to difficulty in recovery of Zn (II) salts. Several catalyst have been reported for the addition of sodium azide to nitriles such as mesoporous ZnS,[25] silica sulfuric acid,[26] $FeCl_3$-SiO_2,[27] $NaHSO_4$-SiO_2,[28] chitosan derived magnetic ionic liquid,[29] $AgNO_3$,[30] CoY zeolite,[31] CAN-HY-zeolite,[32] Zn/Al hydrotalcite,[33] Zn hydroxyapatite,[34] $AlCl_3$,[35] $Et_3N{\cdot}HCl$,[22] TBAF,[36] $Pd(PPh_3)_4$,[37] ZnO,[38] Zn-Cu alloy,[39] $Ln(OTf)_3$ –SiO_2.[47]

The reported catalytic methods are time consuming, with the stringent conditions, and utilizing costly, air sensitive, non- recoverable, toxic metal catalysts (e.g., $Pd(PPh_3)_4$). Therefore, there is a need for the development of a more efficient, convenient, scalable catalyst that addresses these limitations.

Recent reports revealed that the clay or silica based solid acid catalysts played a pivotal role under heterogeneous conditions by catalyzing organic transformations.[40] This is due to tangible benefits like non-corrosiveness, ease of preparation, handling, regeneration, low cost, and insolubility in most of the organic solvents. The catalytic activity of clays is due to their Bronsted as well as Lewis acidic characters in their natural form.[41–43] Fuller's earth is a commercially available, non-toxic, eco-friendly, economic material. These qualities of Fuller's earth makes it safer and suitable for both laboratories as well as industrial processes. Fuller's earth has been used to analyze color additives in food products and as an adsorbent in pharmaceutical & cosmetics. However, to the best of our knowledge, the applications of Fuller's earth for organic

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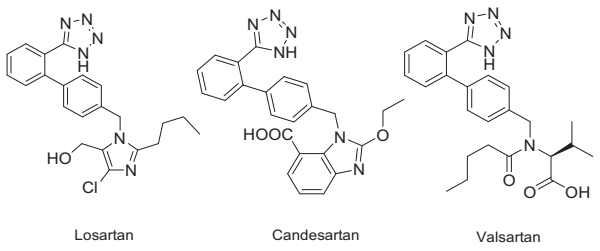


Fig. 1. Drugs of sartan series.

transformation have seldomly reported. Fuller's earth was reported as a catalyst for synthesizing bis(indolyl)methanes.[44] This inspired us to develop a new, eco-friendly activated Fuller's earth as a catalyst. In continuation of our efforts towards the development of eco-friendly green catalytic methodology, we herein report an alternative, simple, and heterogeneous catalyst for the synthesis of 5-aryl 1-*H*-tetrazole.

The Fuller's earth clay was treated with 5% HCl, at 100 °C for 4 h to activate, cooled to room temperature. Insoluble solid was filtered, wash with distilled water till free from acid, dried at 100 °C till constant weight.[48] This treatment increases its adsorption capacity, specific surface area, and pore volume.[45,46]

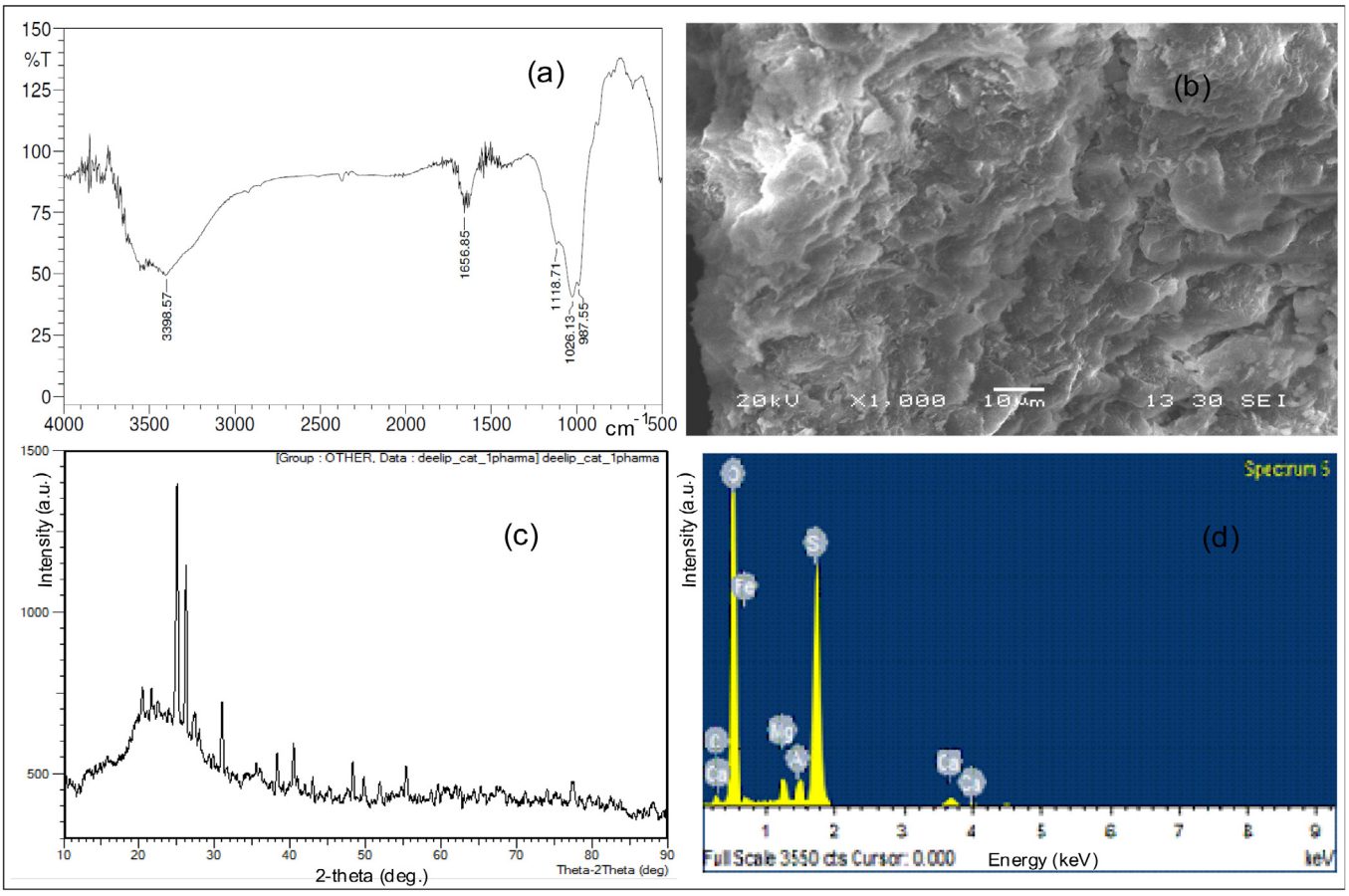
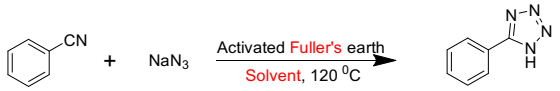


Fig. 2. (a) FTIR spectrum; (b) SEM image; (c) XRD pattern; (d) EDAX.

Table 1
Solvent optimization studies for the synthesis of 5-aryl 1-*H*-tetrazole.



Entry	Catalyst by wt%	Solvent	Temperature (°C)	Time (h)	Yield[a] (%)
1.	10	No solvent	120	12	0
2.	10	Acetonitrile	Reflux	6	0
3.	10	Tetrahydrofuran	Reflux	6	0
4.	10	Water	Reflux	6	18
5.	10	Ethanol	Reflux	6	30
6.	10	DMF	120	1.5	78
7.	10	DMSO	120	1.5	91

[a] Isolated yield.