



Sulfonated carbon/silica composite functionalized Lewis acids for one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles, 3,4-dihydropyrimidin-2(1H)-ones and for Michael addition of indole to α,β -unsaturated ketones

Princy Gupta, Satya Paul*

Department of Chemistry, University of Jammu, Jammu 180 006, India

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ABSTRACT

Novel Lewis acid catalysts were prepared from sulfonated carbon/silica composites derived from starch and silica by treatment with Lewis acids AlCl_3 , SbCl_3 , $\text{Bi}(\text{NO}_3)_3$, ZnCl_2 and FeCl_3 . The catalytic activity of the Lewis acids was evaluated for one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles, 3,4-dihydropyrimidin-2(1H)-ones and for Michael addition of indole to α,β -unsaturated ketones. Different Lewis acids were investigated with a view to select the most effective solid Lewis acid for organic synthesis. All the Lewis acid catalysts were characterized by FTIR, XRD and AAS analysis and the most active catalyst CSC-Star- $\text{SO}_3\text{-AlCl}_2$ was also characterized by TGA, SEM and TEM.

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1. Introduction

Lewis acid catalysts find widespread applications, particularly in chemical industry. Nevertheless several defects such as intractability of separation from products, difficulty of recovery and recycling, generation of acidic waste water during post treatment, high deliquescence, and low product selectivity exist in free Lewis acid catalysts, so limit their applications in industry as well as in academia. In contrast, immobilized Lewis acid catalysts could remove these problems and thus, maximize their value for academia and industrial catalysis. Recently, supported Lewis acid catalysts have been widely used in organic synthesis, e.g. hydroxypapatite supported Lewis acid catalyst has been developed for the transformation of trioses in alcohols [1]; $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ has been described as heterogeneous catalyst with water tolerant Lewis acid sites [2]; silica gel supported aluminium chloride has been reported for the solvent-free synthesis of bis-indolylmethanes [3]; polystyrene supported $\text{Al}(\text{OTf})_3$ was used for the synthesis of acylals from aldehydes [4]; and immobilization of cobalt complex of 1,2-bis(pyridine-2-carboxamido)benzene onto sulfonic

acid functionalized SBA-15 molecular sieves leads to an efficient catalyst for the opening of epoxide ring with amines [5].

Various substituted imidazoles act as inhibitors of p38 MAP kinase [6], glucagon receptors [7], plant growth regulators [8], therapeutic agents [9], antibacterial [10], antitumor [11] and also pesticides [12]. They also serve as useful building blocks for the synthesis of other important materials. Recently, a number of methods using L-proline [13], p-TsOH [14], carbon-based solid acid [15], mercaptopropyl silica [16], preyssler-type heteropolyacid [17], neutral ionic liquid 1-butyl-3-methylimidazolium bromide [18], supported heteropolyacids [19], zinc oxide [20] have been developed for the synthesis of 1,2,4,5-tetrasubstituted imidazoles. Most of the methods for the synthesis of tetrasubstituted imidazoles suffer from one or more disadvantages such as hazardous reaction conditions, complex work-up, strong acidic conditions, poor yields, occurrence of side reactions and use of toxic metal catalysts. Thus, the development of mild method making use of catalysts derived from renewable resources for the synthesis of substituted imidazoles still remains a challenge for organic chemists.

3,4-Dihydropyrimidinones (Biginelli compounds) and their sulfur analogs have been known to possess diverse pharmacological properties such as antiviral, antibacterial, and anti-inflammatory activities [21]. Numerous methods for the synthesis of 3,4-dihydropyrimidinones using different catalysts such as cobalt

* Corresponding author. Tel.: +91 191 2453969; fax: +91 191 2505086.
E-mail address: paul7@rediffmail.com (S. Paul).

hydrogen sulfate [22], nanosized metal oxides [23], sulfated tungstate [24], protic acids [25], Pd mediated C–C coupling strategy [26], tributyl borate [27] have been reported. There is still need to develop a mild and cost-effective method for the synthesis of Biginelli compounds.

Indole is a privileged heterocyclic ring [28–30]. Many biologically active compounds possess 3-substituted indole moieties [31]. Michael addition of indoles to α,β -unsaturated ketones is an important approach to this class of molecules [32,33]. Generally this has been achieved with base catalysis, which becomes problematic if base sensitive groups are present. Thus, acid catalyzed Michael addition of indole to α,β -unsaturated ketones is currently under active investigation. Recently, many catalysts such as polyvinyl sulfonic acid [34], metal halide hydrates [35], task-specific ionic liquids [36], bimetallic iron–palladium catalysts [37] have been reported for the Michael addition of indole to α,β -unsaturated ketones.

In the past few years, carbon based solid acid catalysts [38–46] prepared from the sulfonation of carbonized biomaterials have been extensively used in organic syntheses. Recently, sulfonated silica/carbon hybrids [47–49] have attracted more attention due to more activity and selectivity. Recently, Peng et al. [50] have reported carbon based Lewis acid catalyst derived from sucrose for Michael addition of indole to α,β -unsaturated ketones.

Herein, we report the simple preparation of sulfonated carbon/silica composite functionalized Lewis acids derived from renewable bio-material, starch. To the best of our knowledge it is the first example of the preparation of such Lewis acid catalysts. Here, it is important to mention that we choose starch as the carbon source since the amount of amylopectin ratio in the starch is important for the formation of small polycyclic aromatic rings that provide anchoring sites for $-\text{SO}_3\text{H}$ groups, which affects the final catalyst activity [51]. The catalytic activity of these Lewis acids was evaluated for one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles, 3,4-dihydropyrimidin-2(1H)-ones and for Michael addition of indole to α,β -unsaturated ketones. The present work represents continuation of our studies on the development of green procedures for acid catalyzed organic reactions [52–55].

2. Experimental

2.1. General remarks

The chemicals used were purchased from Aldrich chemical company and Merck. The products were characterized by their spectral data and comparison of their physical data with those of known samples. The ^1H NMR data were recorded in CDCl_3 or $\text{CDCl}_3 + \text{DMSO}-d_6$ on Bruker DPX 200 (200 MHz) spectrometer using TMS as an internal standard. The FTIR spectra were recorded on Perkin-Elmer FTIR spectrophotometer using KBr windows and mass spectral data were recorded on Bruker Esquires 3000 (ESI). XRD diffraction patterns were determined on Bruker AXSD8 X-ray diffraction spectrometer and SEM using Jeol make T-300 Scanning Electron Microscope. Transmission Electron Micrographs (TEMs) were recorded on H7500 Hitachi. The amount of sulfur in sulfonated carbon/silica composite was determined by elemental analysis on Elementar Analysensysteme GmbH VarioEL. Thermal analysis was carried out on DTG-60 Shimadzu make thermal analyzer. The amount of the metals in Lewis acid catalysts was determined by stirring the sample in dil. HNO_3 and subjecting to AAS analysis on GBC Avanta-M Atomic Absorption Spectrometer manufactured by GBC Scientific agencies. All yields refer to isolated yields.

2.2. General procedure for the preparation of sulfonated carbon/silica composite functionalized Lewis acids

Sulfonated carbon/silica composite was prepared according to our recently reported method [56] with slight modifications.

Carbon/silica composite was prepared by taking the mixture of silica (K100, 0.063–0.200 mm) and starch in the ratio of 1:1.3 in a round-bottom flask (25 mL) and then heating this mixture (of silica and starch) at 353 K for 10 h, followed by incomplete carbonization at 673 K under nitrogen for 8 h. During partial carbonization, white color got changed to black, indicating that carbon/silica composite was formed. This was then sulfonated by heating in concentrated sulfuric acid (>96 wt%) at 423 K for 8 h under N_2 atmosphere. The composite material obtained was then washed repeatedly with hot distilled water (>353 K) until sulfate anions were no longer detected in the filtered water. Sulfonated carbon/silica composite was finally dried in an oven at 373 K for 2 h and was then converted into sulfonated carbon/silica functionalized Lewis acids through anion metathesis. The solid acid (1 g) was treated with AlCl_3 or SbCl_3 or $\text{Bi}(\text{NO}_3)_3$ or ZnCl_2 or FeCl_3 (0.00263 mol) in acetonitrile (10 mL) at reflux temperature for 24 h. After cooling to room temperature, the mixture was filtered, washed with acetonitrile and dried under vacuum and finally kept at 90 °C overnight. In order to remove any physisorbed Lewis acid, the catalyst was conditioned by refluxing for 12 h each in xylene at 130 °C (2×2 h), ethanol at 78 °C (2×2 h) and acetonitrile at 80 °C (2×2 h). Finally, the catalyst was dried at 90 °C overnight.

2.3. General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazoles

To a mixture of aldehyde (1 mmol), benzil (1 mmol), primary amine (1 mmol) and ammonium acetate (1.5 mmol) in a round-bottom flask (25 mL), CSC-Star- SO_3AlCl_2 (0.2 g, 9 mol% Al) and ethanol (7 mL) was added and reaction mixture was stirred at 80 °C for an appropriate time (Table 1). After completion of the reaction (monitored by TLC), the reaction mixture was filtered off at the reaction temperature and residue was washed with hot ethyl acetate (3×10 mL). The organic layer was washed with water and dried over anhyd. Na_2SO_4 . Finally, the product was obtained after removal of the solvent under reduced pressure and purified by crystallization with EtOAc: pet ether. The catalyst was washed with double distilled water followed by CH_2Cl_2 (2×10 mL). It was dried at 90 °C for 2 h and reused for subsequent reactions.

2.4. General procedure for the synthesis of 3,4-dihydropyrimidin-(1H)-2-ones

To a mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1 mmol) in a round-bottom flask (25 mL), CSC-Star- SO_3AlCl_2 (0.2 g, 9 mol% Al) and acetonitrile (7 mL) was added and reaction mixture was stirred at 80 °C for an appropriate time (Table 1). On completion (monitored by TLC), the reaction mixture was filtered off at the reaction temperature and residue was washed with hot ethyl acetate (3×10 mL). The organic layer was washed with water and dried over anhydrous Na_2SO_4 . Finally, the product was obtained after removal of the solvent under reduced pressure and purified by crystallization with EtOAc: pet ether. The catalyst was washed with double distilled water followed by CH_2Cl_2 (2×10 mL). It was dried at 90 °C for 2 h and reused for subsequent reactions.

2.5. General procedure for Michael addition of indole to α,β -unsaturated ketones

To a mixture of indole (1.2 mmol) and α,β -unsaturated ketone (1 mmol) in a round-bottom flask (25 mL), CSC-Star- SO_3AlCl_2 (0.2 g, 9 mol% Al) and toluene (7 mL) was added and reaction mixture was stirred at 110 °C for an appropriate time (Table 1). On completion (monitored by TLC), the reaction mixture was filtered off at the reaction temperature and residue was washed with hot ethyl acetate

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