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Preparation and characterization of Lewis acid grafted sulfonated carbon@titania composites for the multicomponent synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazoles and benzoxanthenones under solvent-free conditions

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ABSTRACT

A series of novel and highly efficient Lewis acids covalently grafted over sulfonic acid functionalized carbon@titania composites were successfully synthesized via sulfonation of carbon@titania composites followed by treatment with different Lewis acids like $AlCl_3$, $FeCl_3$, $SbCl_3$, $SnCl_2$, $Cu(OAc)_2$ and $Bi(NO_3)_3$. The utility of the developed catalysts was explored for the synthesis of a diverse range of 4*H*-pyrimido[2,1-*b*]benzothiazoles and benzoxanthenones, and among various catalysts, $C/TiO_2–SO_3–SbCl_2$ was found to be the most active. We report here the synthesis of five novel compounds and the structure of one of the compounds has also been confirmed by single-crystal X-ray diffraction. All the five prepared composites were characterized by FTIR and ICP-AES analysis, whereas the most active one, $C/TiO_2–SO_3–SbCl_2$ was further characterized by XRD, EDX, CHNS, SEM, TEM, HRTEM and TGA. The catalyst can be recovered and reused for atleast five runs without any significant impact on catalytic activity and selectivity. The high catalytic activity, thermal stability, simple recovery and reusability, and eco-friendly nature of the catalyst makes the present method to be particularly attractive from the view point of green chemistry.

1. Introduction

Lewis acid catalysts such as $AlCl_3$, BF_3, and transition metal halides find wide applications in the production of industrially important chemicals, including polymers and pharmaceuticals [1]. However, these homogeneous catalysts are highly toxic, moisture sensitive, show air intolerance and expensive. In addition, the recovery and reuse of homogeneous Lewis acid catalysts is an extremely formidable obstacle. Recently, the use of Lewis acids supported on "inert" carriers has received considerable importance [2–5]. The improved activity, greater selectivity, ease of handling, enhanced reaction rates, simple workup and recyclability are other common features that make the use of supported Lewis acids as attractive alternatives to conventional homogeneous reagents. For this purpose, biomass-derived porous carbons have been found to be potential supports for the preparation of carbon-supported catalysts with a wide range of catalytic applications. Such carbonaceous catalysts are environmentally benign and could provide a cost-competitive advantage as compared to existing heterogeneous catalysts. Excellent physical properties of carbon materials such as chemically inert nature, stability against various chemical environments, low cost, hydrophobicity and tunable surface properties make such catalytic systems compatible with diverse catalysis reactions [6–9]. Recently, carbon based materials have been dispersed over inorganic oxides like silica, titania etc. to develop hybrid composite materials that show synergistic effect of both the organic and inorganic support material on the catalytic performance of the final catalyst [10–14]. Such hybrid materials show enhanced chemical and thermal stability, higher catalytic activity and availability of active surface groups for the linkage of the active catalytic species.

Multicomponent reactions (MCRs) have become powerful tools in organic, combinatorial and medicinal chemistry, and have attracted much attention from synthetic organic chemists because they can build complex molecules with a diverse range of complexities from readily available starting materials [15–18]. 4*H*-Pyrimido[2,1-*b*]benzothiazole derivatives are an important class of fused heterocycles due to their broad range of potential biological activities, as well as their importance in the preparation of drug molecules and natural products [19–23]. Xanthenes and benzox-

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anthenones represent the most common structural motifs found in several natural products and synthetic bioactive compounds. Over the recent years, these have attracted considerable attention due to their diverse biological properties as well as their use as dyes and fluorescent materials [24–27]. Synthetic strategies mediated through the use of variable catalytic systems have been reported in literature for the synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazoles [28–31] and benzoxanthenones [32–43]. Many of these synthetic methods, however, have limitations such as harsh reaction conditions, long reaction time, expensive catalysts, and generation of noticeable amount of side products. Thus, there is an ample scope for the development of new greener synthetic protocols to assemble such scaffolds.

In this context, considering the broad applicability of carbon based organic–inorganic hybrid materials, we have designed and synthesized novel and sustainable catalytic system utilizing carbon@titania composites functionalized by sulfonic acid as the support material for the immobilization of different Lewis acids. The catalytic activity of the solid Lewis acid catalysts has been explored for the one-pot multicomponent synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazoles and benzoxanthenones under solvent-free conditions. The aim of this protocol is to highlight the synergistic effect of the combined use of multicomponent coupling reactions under solvent-free conditions and application of solid Lewis acid catalyst supported on carbon@titania composites for the development of new eco-friendly strategy for heterocyclic synthesis.

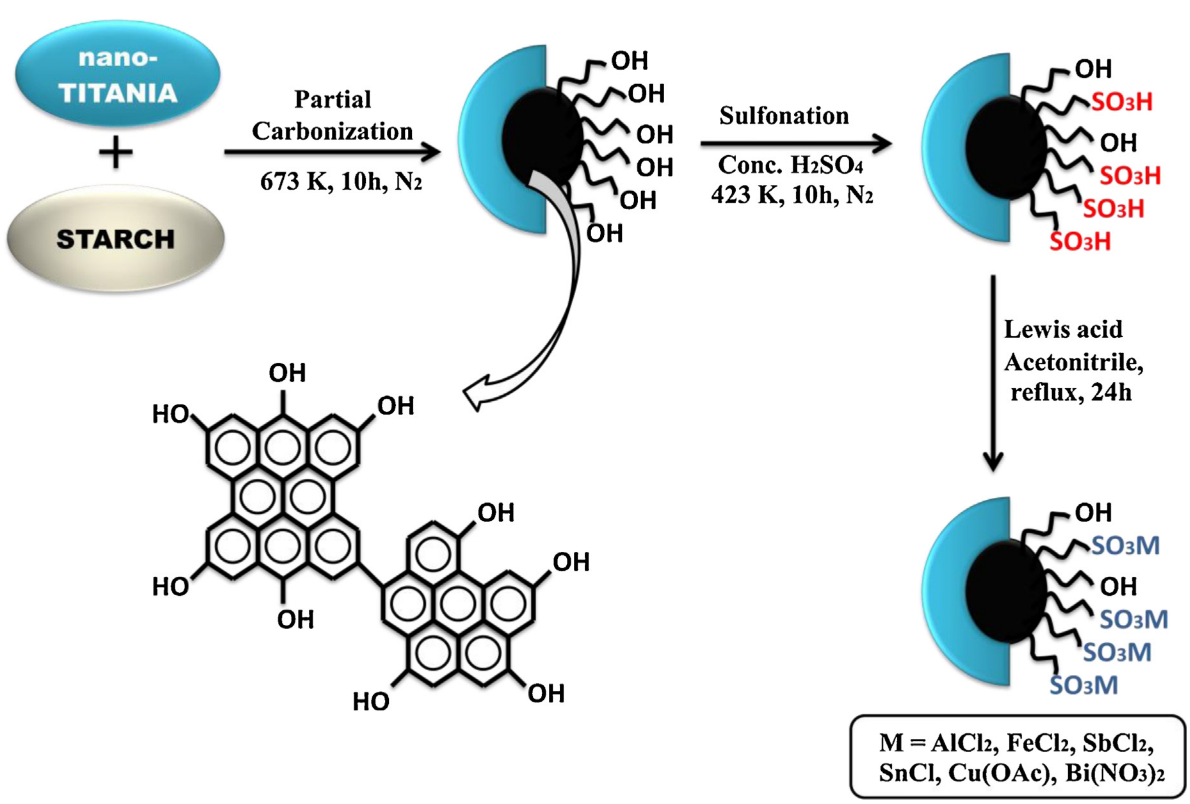
2. Experimental

2.1. Reagents and instrumentation

All starting materials were purchased from commercial sources and used without further purification. The ^{1}H and ^{13}C NMR data were recorded in $CDCl_3$ or DMSO-d_6 or $CDCl_3$+DMSO-d_6 on Bruker Avance III (400 MHz) spectrometer. The FTIR spectra were recorded on Thermo Nicolet, Avatar 370 spectrophotometer, XRD was recorded in 2θ range of 10–80° on Bruker AXS D8 Advance and mass spectral data on Bruker Esquires 3000 (ESI). CHNS analysis was recorded on ThermoFinnigan FLASH EA 1112 series. SEM images were recorded using JEOL Model JSM-6390LV Scanning Electron Microscope, Transmission Electron Micrographs (TEM) were recorded on Philips CM-200. EDX analysis was carried out using JEOL Model JED-2300 and TGA was recorded on PerkinElmer, Diamond TG/DTA.

2.2. Preparation and characterization of Lewis acid grafted sulfonated carbon@titania composites

Initially, carbon@titania composites were prepared by the partial carbonization of starch in the presence of nano-titania leading to the formation of amorphous carbon@titania composites. Thereafter, the functionalization of the as prepared composites with sulfonic acid group was done using conc. sulfuric acid followed by treatment with different lewis acids viz $AlCl_3$, $FeCl_3$, $SbCl_3$, $SnCl_2$, $Cu(OAc)_2$, $Bi(NO_3)_3$, thereby forming respective Lewis acid grafted sulfonated carbon@titania composites [C/TiO_2–SO_3–$AlCl_2$, C/TiO_2–SO_3–$FeCl_2$, C/TiO_2–SO_3–$SbCl_2$, C/TiO_2–SO_3–SnCl, C/TiO_2–SO_3–Cu(OAc), C/TiO_2–SO_3–$Bi(NO_3)_2$]. Among the different inorganic oxides available, we have used titanium dioxide because of its unique surface properties. Besides, titanium dioxide has been shown to exhibit promising electrochemical properties, high photocatalytic activity, high chemical and thermal stability, easy commercial availability and non-toxicity [44–45]. Titania and its composites have usually been studied for their photocatalytic properties [46–49], whereas in the present work titania based carbon composites have been studied for catalytic activity.



Scheme 1. General scheme for the synthesis of Lewis acid grafted sulfonated carbon@titania composites.