



# 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 $\alpha,\beta$ -unsaturated ketones

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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  $\text{AlCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{ZnCl}_2$  and  $\text{FeCl}_3$ . 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  $\alpha,\beta$ -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

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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  $\alpha,\beta$ -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  $\alpha,\beta$ -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  $\alpha,\beta$ -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  $\alpha,\beta$ -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  $\alpha,\beta$ -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  $^1\text{H}$  NMR data were recorded in  $\text{CDCl}_3$  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.  $\text{HNO}_3$  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  $\text{N}_2$  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  $\text{AlCl}_3$  or  $\text{SbCl}_3$  or  $\text{Bi}(\text{NO}_3)_3$  or  $\text{ZnCl}_2$  or  $\text{FeCl}_3$  (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 ( $2 \times 2$  h), ethanol at 78 °C ( $2 \times 2$  h) and acetonitrile at 80 °C ( $2 \times 2$  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- $\text{SO}_3\text{AlCl}_2$  (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 ( $3 \times 10$  mL). The organic layer was washed with water and dried over anhyd.  $\text{Na}_2\text{SO}_4$ . 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  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  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- $\text{SO}_3\text{AlCl}_2$  (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 ( $3 \times 10$  mL). The organic layer was washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . 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  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  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 $\alpha,\beta$ -unsaturated ketones

To a mixture of indole (1.2 mmol) and  $\alpha,\beta$ -unsaturated ketone (1 mmol) in a round-bottom flask (25 mL), CSC-Star- $\text{SO}_3\text{AlCl}_2$  (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

**Table 1**

CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> catalyzed one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles at 80 °C in ethanol<sup>a</sup>, 3,4-dihydropyrimidin-2(1H)-ones at 80 °C in acetonitrile<sup>b</sup> and Michael addition of indole to  $\alpha,\beta$ -unsaturated ketones<sup>c</sup> at 110 °C in toluene.

Product	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Time (h)	Yield (%) <sup>d</sup>	m.p./lit. m.p. (°C)
2a	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	8	96	216–217/216–218 [14]
2b	4-ClC <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	10	94	164–165/161–163 [13]
2c	4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	7.5	95	190–191/191–193 [13]
2d	4-OHC <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	7	94	284–285/284–286 [13]
2e	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	10	94	162–163/163–165 [13]
2f	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	8	93	165–166/167–168 [13]
2g	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	8	93	188–189/187–189 [13]
2h	4-(OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	10	94	182–183/184–185 [14]
2i	4-(OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	10	95	162–163/164–165 [13]
3a	C <sub>6</sub> H <sub>5</sub>	H	H	11.5	95	208–209/209–210 [53]
3b	4-(OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	H	H	10	95	200–201/201–202 [53]
3c	4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub>	H	H	10	96	207–208/207–209 [53]
3d	4-OH-3-(OMe)C <sub>6</sub> H <sub>3</sub>	H	H	10	95	231–232/231–232 [53]
3e	C <sub>6</sub> H <sub>5</sub> CH=CH	H	H	11	96	243–244/245–246 [53]
3f	2-Furfuryl	H	H	11.5	94	208–209/208–210 [53]
3g	4-ClC <sub>6</sub> H <sub>4</sub>	H	H	10.5	94	215–216/216–217 [53]
3h	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	10.5	93	248–249/248–250 [61]
4a	C <sub>6</sub> H <sub>5</sub> CH=CH	C <sub>6</sub> H <sub>5</sub>	H	12	85	126–127/127–128 [62]
4b	4-ClC <sub>6</sub> H <sub>4</sub> CH=CH	C <sub>6</sub> H <sub>5</sub>	H	13.5	85	118–119/118–121 [62]
4c	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH=CH	C <sub>6</sub> H <sub>5</sub>	H	13	85	129–130/130–131 [62]
4d	4-(OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH=CH	C <sub>6</sub> H <sub>5</sub>	H	12.5	82	122–123/124–125 [60]
4e	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH=CH	4-ClC <sub>6</sub> H <sub>4</sub>	H	13	84	146–147/146–149 [62]

<sup>a</sup> Reaction conditions: aldehyde (1 mmol), benzil (1 mmol), aromatic amine (1 mmol), NH<sub>4</sub>OAc (1.5 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) at 80 °C in ethanol.

<sup>b</sup> Reaction conditions: aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) at 80 °C in acetonitrile.

<sup>c</sup> Reaction conditions:  $\alpha,\beta$ -unsaturated ketone (1 mmol), indole (1.2 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) at 110 °C in toluene.

<sup>d</sup> Isolated yields.

(3 × 10 mL). The organic layer was washed with water and dried over anhyd. Na<sub>2</sub>SO<sub>4</sub>. The product was obtained after removal of the solvent under reduced pressure and passing through column of silica gel and elution with EtOAc: pet ether. The catalyst was washed with double distilled water followed by CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). It was dried at 90 °C for 2 h and reused for subsequent reactions.

The products were confirmed by IR, <sup>1</sup>H NMR, mass spectral data, microanalytical data and comparison with authentic samples obtained commercially or prepared according to literature methods.

### 2.5.1. Spectral data of some selected compounds

1-Benzyl-2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (2b): IR (KBr,  $\nu_{\max}$  in cm<sup>-1</sup>): 3055, 2930, 1600, 1419; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.12 (s, 2H, CH<sub>2</sub>Ph), 6.90–7.90 (m, 19H, ArH); ESI-MS (*m/z*): 421 (M<sup>+</sup>+1); Anal. Calcd. for C<sub>28</sub>H<sub>21</sub>ClN<sub>2</sub>: C, 79.84; H, 5.03; N, 6.66. Found: C, 79.91; H, 5.09; N, 6.62.

2-(4-Methylphenyl)-1,4,5-triphenyl-1H-imidazole (2g): IR (KBr,  $\nu_{\max}$  in cm<sup>-1</sup>): 3047, 2920, 1660, 1586; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.25 (s, 3H, CH<sub>3</sub>), 7.01–7.35 (m, 19H, ArH); ESI-MS (*m/z*): 387 (M<sup>+</sup>+1); Anal. Calcd. for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.03; H, 5.81; N, 7.16.

Ethyl-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one-5-carboxylate (3b): IR (KBr,  $\nu_{\max}$  in cm<sup>-1</sup>): 3395, 3248, 3100, 2968, 1700, 1661, 1268, 1098; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.03–1.29 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>), 3.84 (s, 3H, OCH<sub>3</sub>), 3.94–4.15 (q, 2H, CH<sub>2</sub>CH<sub>3</sub>), 5.51 (s, 1H, C4-H), 6.83–6.93 (d, 2H, ArH), 7.25–7.35 (d, 2H, ArH), 7.69 (bs, 1H, NH), 9.17 (bs, 1H, NH); ESI-MS (*m/z*): 290 (M<sup>+</sup>); Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub>: C, 62.06; H, 6.20; N, 9.65. Found: C, 62.09; H, 6.18; N, 9.64.

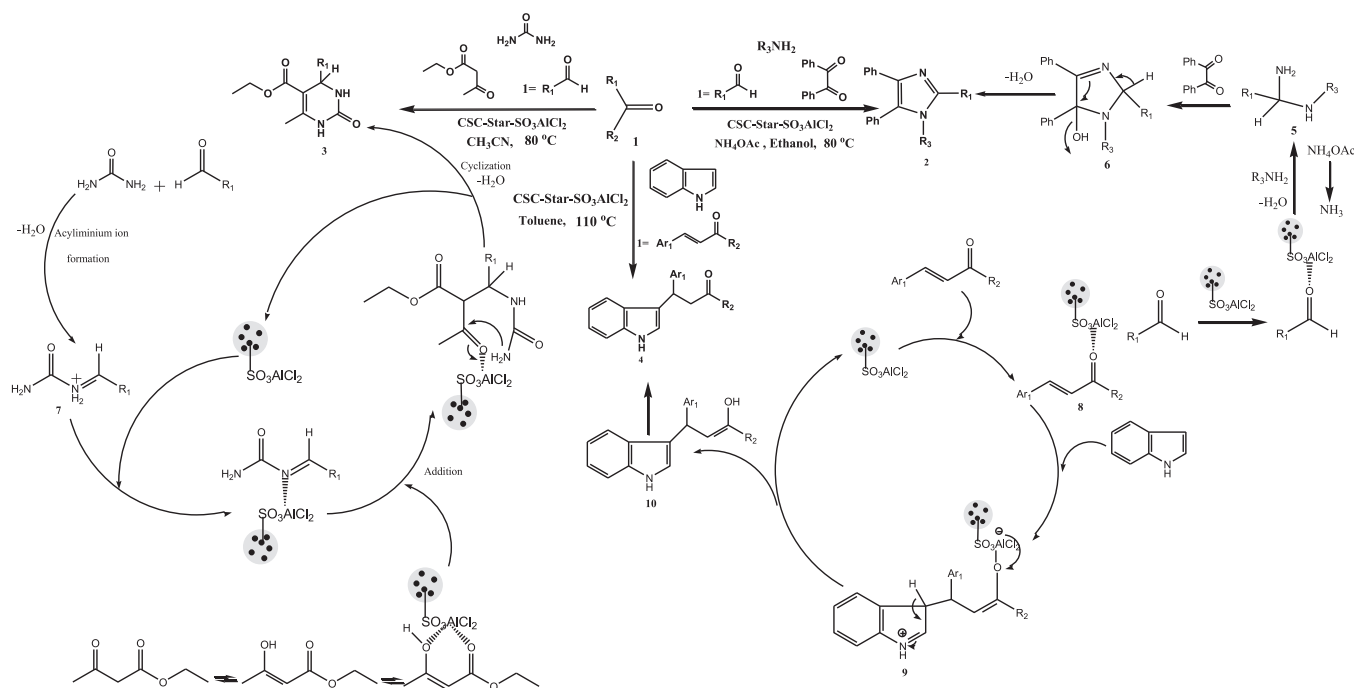
3-(3-Indolyl)-1-phenyl-3-(4-methylphenyl)propan-1-one (4c): IR (KBr,  $\nu_{\max}$  in cm<sup>-1</sup>): 3395, 3090, 3020, 2965, 2920, 2860, 1955, 1890, 1595, 1580, 1550, 1500, 1480, 1450, 1410, 1390, 870, 770, 720, 680; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.25 (s, 3H, CH<sub>3</sub>), 3.85 (dd, 2H, CH<sub>2</sub>), 5.00 (t, 1H, CH), 7.01–7.85 (m, 14H, ArH), 8.00 (bs, 1H, NH); ESI-MS (*m/z*): 339 (M<sup>+</sup>); Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>ON: C, 84.95; H, 6.19; N, 4.12. Found: C, 84.91; H, 6.21; N, 4.14.

## 3. Results and discussion

### 3.1. Catalyst preparation and characterization

In the first step, sulfonated carbon/silica composite was prepared by the partial carbonization of starch in the presence of silica which acts as a precursor, followed by dehydration and dissociation of –C–O–C– linkages, leading to the formation of polycyclic aromatic carbon rings and the amorphous carbon structure. The aromatic polycyclic rings were then sulfonated with concentrated sulfuric acid. The sulfonated solid acid was then transformed into Lewis acid catalysts (CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-SbCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-Bi(NO<sub>3</sub>)<sub>2</sub>, CSC-Star-SO<sub>3</sub>-ZnCl, CSC-Star-SO<sub>3</sub>-FeCl<sub>2</sub>) through anion metathesis. Lewis acid catalysts were characterized by FTIR, XRD and AAS. The most active Lewis acid catalyst CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> was also characterized by TGA, SEM and TEM.

XRD patterns of sulfonated carbon/silica functionalized Lewis acids showed broad diffraction peaks at low diffraction angles  $2\theta = 10\text{--}30^\circ$ , C(002), attributed to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion (Fig. S1, see Supporting information) [57]. The FTIR spectra of sulfonated carbon/silica composite showed bands at 1625 and 1390 cm<sup>-1</sup> which were assigned to aromatic C=C stretching modes in polyaromatic rings. The bands at 2929 cm<sup>-1</sup> were due to the phenolic –OH groups in the aromatic rings. The sulfonated carbon/silica composite also showed the absorption bands from 1450 to 1460 cm<sup>-1</sup> (due to asymmetric stretching of SO<sub>2</sub>) and between 1100 and 1110 cm<sup>-1</sup> (due to symmetric stretching of SO<sub>2</sub>), which indicated that solid acid possesses SO<sub>3</sub>H groups. FTIR of the sulfonated carbon/silica functionalized Lewis acids again showed bands at 1620 and 1350 cm<sup>-1</sup> due to aromatic C=C stretching modes. The asymmetric and symmetric stretching bands of SO<sub>2</sub> in Lewis acid catalysts has shifted to 1430–1445 cm<sup>-1</sup> and 1082–1089 cm<sup>-1</sup>, respectively owing to the decreased electron density of S–O bond, which was caused by the formation of S–O–M bond. The amount of metals loaded onto sulfonated carbon/silica functionalized Lewis acids was determined by stirring the catalyst in dilute nitric acid and then subjecting to AAS analysis. It was



Scheme 1.

found that 0.45 mmol Al, 0.43 mmol Sb, 0.41 mmol Fe, 0.40 mmol Bi and 0.38 mmol Zn was present per gram of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-SbCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-FeCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-Bi(NO<sub>3</sub>)<sub>2</sub> and CSC-Star-SO<sub>3</sub>-ZnCl, respectively.

The stability of the most active Lewis acid catalyst CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> was examined by thermal analysis. The curve was divided into regions corresponding to different weight loss ranges. The first region between 80 and 100 °C displayed a weight loss which may be attributed to loss of residual solvent and water trapped onto the surface of the catalyst. A second region in the curve showed weight loss from 250 to 700 °C, which was attributed to the loss of organic material including -SO<sub>3</sub>AlCl<sub>2</sub> and polycyclic aromatic carbon chains (Fig. S2, see Supporting information). Thus, the catalyst is stable up to 250 °C and it is safe to carry out the reaction at 80 and 110 °C. The microstructure and morphology of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> was also studied using Scanning Electron Microscope (SEM). SEM images (Fig. S3, see Supporting information) showed that catalyst is a homogeneous powder with porous structure. The TEM micrographs (Fig. S4, see Supporting information) showed that catalyst has composite type nature in which carbonized biomaterials are loaded into the mesopores of silica and metal species

Table 2

Effect of the sulfonated carbon-silica composite functionalized Lewis acids on the synthesis of 1,2,4,5-tetrasubstituted imidazoles, 3,4-dihydropyrimidin-2(1H)-ones and for Michael addition of indole to  $\alpha,\beta$ -unsaturated ketones.

Entry	Catalyst <sup>a</sup>	Imidazoles <sup>b</sup>		DHPMs <sup>c</sup>		Michael addition <sup>d</sup>	
		Time (h)	Yield (%) <sup>e</sup>	Time (h)	Yield (%) <sup>e</sup>	Time (h)	Yield (%) <sup>e</sup>
1	CSC-Star-SO <sub>3</sub> AlCl <sub>2</sub>	8	96	10	95	13	85
2	CSC-Star-SO <sub>3</sub> SbCl <sub>2</sub>	9	85	10	80	13	80
3	CSC-Star-SO <sub>3</sub> Bi(NO <sub>3</sub> ) <sub>2</sub>	10	82	11	75	13	75
4	CSC-Star-SO <sub>3</sub> ZnCl	11	85	11	85	13	75
5	CSC-Star-SO <sub>3</sub> FeCl <sub>2</sub>	9	80	10	80	13	70

<sup>a</sup> CSC-Star-SO<sub>3</sub>AlCl<sub>2</sub>, catalyst prepared from anhyd. AlCl<sub>3</sub>; CSC-Star-SO<sub>3</sub>SbCl<sub>2</sub>, anhyd. SbCl<sub>3</sub>; CSC-Star-SO<sub>3</sub>Bi(NO<sub>3</sub>)<sub>2</sub>, anhyd. Bi(NO<sub>3</sub>)<sub>3</sub>; CSC-Star-SO<sub>3</sub>ZnCl, anhyd. ZnCl<sub>2</sub>; CSC-Star-SO<sub>3</sub>FeCl<sub>2</sub>, anhyd. FeCl<sub>3</sub>.

<sup>b</sup> Reaction was carried out by stirring a mixture of benzaldehyde (1 mmol), benzil (1 mmol), aniline (1 mmol) NH<sub>4</sub>OAc (1.5 mmol) and sulfonated carbon-silica composite functionalized Lewis acid (9 mol% metal) at 80 °C in ethanol.

<sup>c</sup> Reaction was carried out by stirring a mixture of anisaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1 mmol) and sulfonated carbon-silica composite functionalized Lewis acid (9 mol% metal) at 80 °C in acetonitrile.

<sup>d</sup> Reaction was carried out by stirring a mixture of 3-(4-methylphenyl)-1-phenyl propenone (1 mmol), indole (1.2 mmol) and sulfonated carbon-silica composite functionalized Lewis acid (9 mol% metal) at 110 °C in toluene.

<sup>e</sup> Isolated yields.

are located on carbon particles inside these composite materials.

### 3.2. Catalyst testing for the synthesis of 1,2,4,5-tetrasubstituted imidazoles, 3,4-dihydropyrimidin-2(1H)-ones and Michael addition of indole to $\alpha,\beta$ unsaturated ketones

1,2,4,5-Tetrasubstituted imidazoles were synthesized by stirring a mixture of aldehyde, benzil, primary amine and ammonium acetate at 80 °C in ethanol in the presence of sulfonated carbon/silica functionalized Lewis acids (Scheme 1). To select the appropriate Lewis acid catalyst, benzaldehyde and aniline were selected as the test substrates, and the reaction was carried out with benzil and ammonium acetate using CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-SbCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-Bi(NO<sub>3</sub>)<sub>2</sub>, CSC-Star-SO<sub>3</sub>-ZnCl, CSC-Star-SO<sub>3</sub>-FeCl<sub>2</sub> at 80 °C in ethanol. The results are presented in Table 2, which indicated that out of various catalysts, CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> exhibited highest activity. Choice of a solvent plays an important role in multicomponent reactions. To choose the appropriate solvent for this reaction, we carried out the test reaction in a variety of protic and aprotic solvents and ethanol



**Table 3**

Comparison of activity of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> with silica, amorphous carbon, non-sulfonated carbon–silica composite, sulfonated amorphous carbon and sulfonated carbon–silica composite and anhyd. AlCl<sub>3</sub> for imidazole synthesis<sup>a</sup>, dihydropyrimidinone synthesis<sup>b</sup> and Michael addition.<sup>c</sup>

Entry	Catalyst	Imidazoles <sup>a</sup>		DHPMs <sup>b</sup>		Michael addition <sup>c</sup>	
		Time (h)	Yield (%) <sup>d</sup>	Time (h)	Yield (%) <sup>d</sup>	Time (h)	Yield (%) <sup>d</sup>
1	No Catalyst	8	NR <sup>e</sup>	10	NR <sup>e</sup>	13	NR <sup>e</sup>
2	Silica	8	15	10	NR <sup>e</sup>	13	NR <sup>e</sup>
3	Amorphous carbon	8	25	10	20	13	10
4	Non-sulfonated carbon–silica composite	8	30	10	25	13	20
5	Sulfonated amorphous carbon	8	40	10	30	13	35
6	Sulfonated carbon–silica composite	8	50	10	40	13	40
7	Anhyd. AlCl <sub>3</sub>	4	90	7	90	10	80
8	CSC-Star-SO <sub>3</sub> -AlCl <sub>2</sub>	8	96	10	95	13	85

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), benzil (1 mmol), aniline (1 mmol), NH<sub>4</sub>OAc (1.5 mmol), catalyst (0.2 g) at 80 °C in ethanol.

<sup>b</sup> Reaction conditions: anisaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1 mmol), catalyst (0.2 g) at 80 °C in acetonitrile.

<sup>c</sup> Reaction conditions: 3-(4-methylphenyl)-1-phenyl propenone (1 mmol), indole (1.2 mmol), catalyst (0.2 g) at 110 °C in toluene.

<sup>d</sup> Isolated yields.

<sup>e</sup> No reaction.

was found to be the best solvent in terms of reaction time and yield. The optimum conditions selected are: aldehyde (1 mmol), benzil (1 mmol), primary amine (1 mmol), ammonium acetate (1.5 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) and 80 °C as the reaction temperature in ethanol (7 mL). To demonstrate the generality of the developed protocol, various aldehydes substituted with both electron-withdrawing and electron-releasing groups were chosen and excellent results were obtained (Table 1).

The catalytic activity of Lewis acid catalysts was also studied for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones under liquid phase catalysis (Scheme 1). Anisaldehyde was selected as the test substrate and reaction was carried out using ethyl acetoacetate and urea in the presence of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-SbCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-Bi(NO<sub>3</sub>)<sub>2</sub>, CSC-Star-SO<sub>3</sub>-ZnCl, CSC-Star-SO<sub>3</sub>-FeCl<sub>2</sub> at 80 °C using acetonitrile as the solvent. The results are presented in Table 2, which indicated that the same Lewis acid catalyst, CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> exhibited highest activity. To study the effect of solvent, we carried out this reaction in acetonitrile, water and ethanol and found that acetonitrile gave the best results for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones. The optimum conditions selected are: aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) and 80 °C as the reaction temperature using acetonitrile (7 mL) as the reaction medium. To demonstrate the generality of the developed protocol, various aldehydes possessing both electron-withdrawing and electron-releasing groups were subjected to reaction under selected conditions and excellent results were obtained (Table 1).

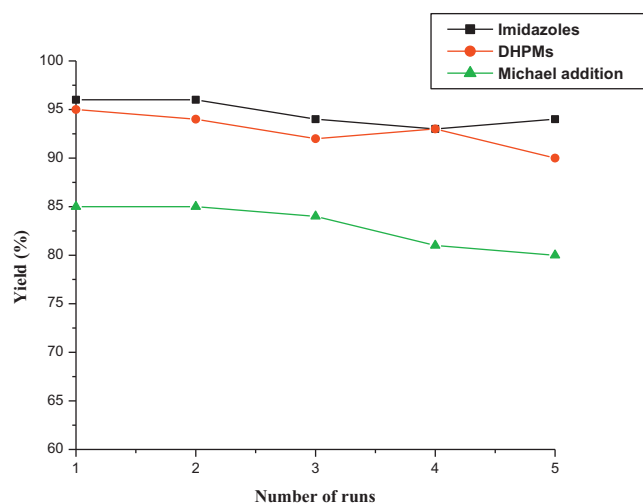
The catalytic activity of sulfonated carbon/silica functionalized Lewis acids was also evaluated for the Michael addition of indole to  $\alpha,\beta$ -unsaturated ketones, which is an excellent method for the generation of library of 3-substituted indoles (Scheme 1). 3-(4-Methylphenyl)-1-phenyl propenone and indole were selected as the test substrates and the reaction was carried out using CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-SbCl<sub>2</sub>, CSC-Star-SO<sub>3</sub>-Bi(NO<sub>3</sub>)<sub>2</sub>, CSC-Star-SO<sub>3</sub>-ZnCl, CSC-Star-SO<sub>3</sub>-FeCl<sub>2</sub> at 110 °C in toluene (Table 2). Among various solvents (toluene, water and acetonitrile), best results were found in toluene. Different  $\alpha,\beta$ -unsaturated ketones were selected and good results were obtained (Table 1) which indicated the scope and generality of the developed protocol.

To optimize the amount of most active catalyst, we carried out the reactions (Table 1, products 2a, 3b and 4c) using different amounts of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, i.e. 0.050 g (2.25 mol% Al), 0.1 g (4.5 mol% Al), 0.15 g (6.75 mol% Al) and 0.2 g (9 mol% Al) and it was found that the best results in terms of reaction time and yield were obtained with 0.2 g (9 mol% Al) of the catalyst.

In order to compare the activity of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> with silica, amorphous carbon, non-sulfonated carbon–silica composite, sulfonated amorphous carbon and sulfonated carbon–silica composite and anhyd. AlCl<sub>3</sub>, benzaldehyde and aniline (for imidazole), anisaldehyde (for dihydropyrimidinone) and 3-(4-methylphenyl)-1-phenyl propenone (for Michael addition) were selected as the test substrates. The results are presented in Table 3. It was found that anhyd. AlCl<sub>3</sub> under homogeneous conditions gave the best results, but suffers from serious drawbacks like acid treatment at the end of the reaction and production of large amount of waste during work-up and further, non-recyclable under the reaction conditions. So, we have selected heterogeneous CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>, which was superior to all other solid catalysts. Recyclability and operational stability of the CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> was tested in case of product 2a, Table 1; product 3b, Table 1; and product 4c, Table 1 for five consecutive runs (Fig. 1). It was found that CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> could be recycled for five consecutive runs without loss of significant activity.

### 3.3. Proposed mechanisms

Plausible mechanism for the Lewis acid catalyzed synthesis of 1,2,4,5-tetrasubstituted imidazoles has been proposed in Scheme 1.



**Fig. 1.** Recyclability of CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub>. Reaction conditions – imidazoles: benzaldehyde (1 mmol), benzil (1 mmol), aniline (1 mmol), NH<sub>4</sub>OAc (1.5 mmol); CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) at 80 °C in ethanol for 8 h; DHPMs: anisaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) at 80 °C in acetonitrile for 10 h; Michael addition: 3-(4-methylphenyl)-1-phenylpropenone (1 mmol), indole (1.2 mmol), CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> (0.2 g, 9 mol% Al) at 110 °C in toluene for 13 h.

In accordance with the mechanism proposed by Konwar et al. [58], the catalyst CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> increases the electrophilicity of the carbonyl group of the aldehyde. Nucleophilic attack of the nitrogen atoms of ammonia, obtained from NH<sub>4</sub>OAc, and amine on the activated carbonyl group resulted in the formation of intermediate 5. This intermediate in the presence of catalyst condenses with benzil to form intermediate 6, which in turn releases a H<sub>2</sub>O molecule to form 1,2,4,5-tetrasubstituted imidazole 2.

A possible mechanism of Biginelli reaction is shown in Scheme 1. Biginelli reaction consists of two steps: formation of acyliminium ion 7 and addition of β-ketoester to an acyliminium ion followed by cyclization and dehydration steps [59]. The presence of Lewis acid CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> is proposed to accelerate the acyliminium ion formation and addition reaction through a metal enolate formation or coordination to an acyliminium ion.

A proposed mechanism for the Michael addition of indole to α,β-unsaturated ketones is represented in Scheme 1. In accordance with the mechanism proposed by Huang et al. [60], in the first step the catalyst CSC-Star-SO<sub>3</sub>-AlCl<sub>2</sub> coordinates with O atom of α,β-unsaturated ketone to form intermediate 8, the conjugated C=C of which was attacked by the electron-rich β-position of indole to give intermediate 9, the intermediate 9 then follows a H-transformation to give 10 which finally rearranges to 4.

#### 4. Conclusions

In conclusion, we have prepared novel sulfonated carbon/silica functionalized Lewis acids derived from sulfonated carbon/silica composite and their catalytic activity was successfully evaluated for the 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 most active catalyst is thermally stable, green, inexpensive and easy to prepare, could be easily separated from the reaction mixture and recycled several times. Moreover, operational simplicity, high yields and easy work-up procedure are the key advantages of the developed methods.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.10.016.

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