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### **Recyclable Sulfonated Amorphous Carbon Catalyzed Friedel–Crafts** Alkylation of Indoles with α,β-Unsaturated Carbonyl Compounds in Water

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Indole derivatives are currently explored as privileged structures for drug design and discovery owing to their high binding affinity to many receptors.<sup>[1]</sup> Among them, 3-substituted indoles, which are important precursors in the synthesis of many biologically active compounds and natural products, have drawn the most attention.<sup>[2]</sup> They are known to be easily synthesized via Michael-type Friedel-Crafts (F-C) reactions of indoles with  $\alpha,\beta$ -unsaturated carbonyl compounds, in the presence of either Brønsted or Lewis acids.<sup>[3]</sup> However, owing to the homogeneous nature of these conventional acids, large stoichiometric amounts and tedious isolation procedures are required. In view of the increasing emphasis on the use of environmentally friendly processes, solid acid catalysts have been proposed as an attractive alternative to conventional liquid acid catalysts owing to their simple workup, ease of recovery, and reusability.<sup>[4]</sup> To date, several silica-supported solid acid catalysts have been developed and employed in the F-C reaction of indoles with electrondeficient olefins.<sup>[5]</sup> Other heterogeneous catalytic systems, which include nanosized TiO<sub>2</sub>,<sup>[6]</sup> ZrOCl<sub>2</sub>·8H<sub>2</sub>O,<sup>[7]</sup> and heteropolyacids<sup>[8]</sup>, have also been reported. Unfortunately, their heterogeneous nature does not guarantee the consistency of catalytic performance after their recovery.<sup>[5b,8]</sup> In fact, many of the silica-supported catalysts are mechanically unstable in water and consequently not reusable in reality.<sup>[9]</sup> Moreover,

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the use of toxic transition metals and nonbenign solvents still remains as an issue in many of these solid acid catalytic systems. A few years ago, Kobayashi and his co-workers developed a neutral catalytic system by combining silica-supported sodium sulfonate with ionic liquid in water.<sup>[10]</sup> While the neutral system allowed the Michael reaction of acid-labile substrates, the reaction time required was generally longer than that of other solid acid catalysts. Despite the recent advances, there is still a demand for other environmentally friendly and efficient alternatives for the F-C reactions of indoles with  $\alpha$ , $\beta$ -unsaturated carbonyl compounds.

Recently, a novel class of carbon-based solid acids derived from carbohydrates has attracted considerable attention for its potential as an inexpensive, environmentally benign and stable catalyst with high catalytic performance.<sup>[11]</sup> Consisting of flexible polycyclic carbon sheets which bear phenolic hydroxy (-OH), carboxylic acid (-COOH), and sulfonic acid (-SO<sub>3</sub>H) groups, the catalyst can be readily prepared by incomplete carbonization of natural carbohydrates, such as glucose, cellulose, and starch, followed by sulfonation of the resulting amorphous carbon.<sup>[12]</sup> Initially used as a green and sustainable catalyst in the esterification of fatty acids in biodiesel production,<sup>[11c]</sup> it was soon reported to demonstrate high catalytic efficiency in other reactions such as hydrolysis<sup>[12a]</sup> and hydration.<sup>[12b]</sup> Inspired by these reports, we envisaged the use of this carbon-based solid acid in catalyzing F-C alkylation to synthesize 3-substituted indoles in an environmentally benign fashion.<sup>[3g,12a,13]</sup> To the best of our knowledge, this is the first demonstration of carbon-based solid acid in catalyzing carbon-carbon bond formations.

The sulfonated carbon-based solid acid **1a** was prepared according to the literature method.<sup>[11c]</sup> The content of **1a** was determined by elemental analysis, and the result obtained for sulfur content was 1.13 wt%. Since all sulfur atoms in the carbon material were in the form of SO<sub>3</sub>H groups,<sup>[12b]</sup> the density of SO<sub>3</sub>H groups in **1a** was thus estimated to be 0.35 mmol g<sup>-1</sup>. The solid acid was further characterized by X-ray diffraction (XRD). The XRD pattern is in good agreement with the literature,<sup>[12a,b]</sup> showing that the

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prepared solid acid is in the form of amorphous carbon (see the Supporting Information).

The catalytic performance of **1a** was first examined using the F-C reaction of indole with methyl vinyl ketone (MVK) as a model reaction. To our delight, the reaction took place smoothly in water<sup>[3e,14]</sup> at ambient temperature to give isolated product in excellent yield (Table 1, entry 1). Investigation

Table 1. Catalyst screening and optimization of reaction conditions.<sup>[a]</sup>

N +	O catalyst solvent, RT	N N N N N N N N N N N N N N N N N N N
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Entry	Catalyst	Cat. loading [mol %]	Solvent	T [h]	Yield [%] <sup>[b]</sup>
1	1a	1.0	$H_2O$	6	96
2	1a	2.0	$H_2O$	3	96
3	1a	5.0	$H_2O$	1	96
4	1a	10.0	$H_2O$	0.5	94
5 <sup>[c]</sup>	1b	29 mg	$H_2O$	48	43
6 <sup>[c]</sup>	1c	29 mg	$H_2O$	8	95
7	black carbon	29 mg	$H_2O$	24	18
8 <sup>[d]</sup>	1a	5.0	H <sub>2</sub> O/ THF	1	93
9	1a	5.0	THF	1	84
10	1a	5.0	$CH_2Cl_2$	1	79
11	1a	5.0	MeCN	1	77
12	1a	5.0	MeOH	1	66
13	1a	5.0	toluene	1	19
14	$H_2SO_4$	5.0	$H_2O$	1	40
15	$H_2SO_4$	100.0	$H_2O$	1	63

[a] Indole (0.2 mmol) was treated with MVK (0.4 mmol) in solvent (1 mL) at room temperature in the presence of the catalyst. [b] Yields of isolated product after purification. [c] The densities of the phosphoric and perchloric acid groups were not determined. [d]  $H_2O/THF$  in the ratio of 4:1 was used.

shows that the reaction time required for complete conversion is inversely proportional to the amount of 1a loaded (Table 1, entries 1–4). However, along with an accelerated reaction rate, the yield remained consistent at about 94% to 96% as the amount of 1a employed was increased from 2 to 10 mol% (Table 1, entry 4). Thus, 5 mol% of 1a was determined to be the optimal amount of catalyst loading.

Next, phosphonated (1b) and perchlorated carbon solid acid (1c) were synthesized by treating the black amorphous carbon with concentrated phosphoric acid and perchloric acid, respectively. They were investigated for their catalytic efficiencies in the model reaction. Less satisfactory results (Table 1, entries 5 and 6) were obtained than that of sulfonated 1a. This suggested that the presence of  $SO_3H$  groups was crucial to the high catalytic performance of the solid acid. To validate this hypothesis, a non-sulfonated black carbon, the precursor of 1a, was used in a control experiment. As anticipated, a very low yield of product was obtained even after prolonged reaction time (Table 1, entry 7).

We also examined the solvent effect by screening different solvent systems (Table 1, entries 8–13). While the reaction

exhibited the best yield in water, the use of solvent mixture  $H_2O/THF$  in the composition of 4:1 was found to afford a comparably good yield as well (Table 1, entry 8). Other solvents provided less satisfactory results, ranging from low to moderate yields (Table 1, entries 9–13).

Treatment of indole and MVK with 5 mol% of sulfuric acid as catalyst brought forth only a small amount of F-C adducts (Table 1, entry 14). Although we raised the amount of sulfuric acid up to one equivalent, limited increase in the amount of product was observed, giving rise to only a moderate yield of product (Table 1, entry 15). These sluggish results show that **1a** is a superior acid catalyst to its conventional homogeneous counterpart.

Encouraged by the positive results from the preliminary studies, we investigated the efficiency of **1a** in the alkylation of indole and its derivatives with various  $\alpha$ , $\beta$ -unsaturated carbonyl compounds under the optimized conditions. Most reactions proceeded smoothly in either H<sub>2</sub>O or H<sub>2</sub>O/THF solvent mixture to furnish the corresponding Michael adducts in moderate to excellent yields (Table 2). Moreover, the advantage of our catalytic system is that protection of the indole NH functional group is unnecessary.

In view of its environmental and economical advantages, water is the preferred solvent system in the course of our investigation. While some reactions were able to proceed smoothly in water to afford excellent yields, others were more sluggish as shown by their prolonged reaction times and the unsatisfactory yields. Poor solubility of the substrates and products in water, especially those of higher complexity, is probably the reason behind these results. We would then opt for an alternative solvent system of  $H_2O/THF$  in the composition of 4:1, which gave comparable good results in our earlier screening of solvents. As anticipated, a remarkable improvement in both the reaction time and yield of isolated product were observed when we switched to this solvent system.

The reaction of indole and its derivatives with MVK proceeded smoothly at ambient temperature in the presence of 5 mol% of solid acid catalyst **1a** to give 85–96% yield of isolated product without side reactions of dimerization or polymerization (Table 2, entries 1–5). It is noteworthy that both electronic and architectural modification of the indole aromatic ring could be accomplished without compromising the good yield. The excellent yield (91%) could also be achieved in the Michael reaction of indole with 4-hexen-3-one (Table 2, entry 6). After all, the Michael acceptor employed is much more sterically hindered in comparison to MVK owing to the elongation of the aliphatic chain. Reactions of various indole derivatives with 4-hexene-3-one also gave satisfactory results (Table 2, entries 7–10).

To further validate the effectiveness of **1a** in promoting F-C reaction of indole with unreactive electron-deficient olefins, several Michael acceptors which are notorious for their poor reactivity to nucleophilic attack were employed (Table 2, entries 11–15). Among them, chalcone and  $\beta$ -nitrostyrene gave satisfactory yields of Michael adducts (Table 2, entries 11 and 12). Other substrates such as  $\alpha$ , $\beta$ -unsaturated

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Table 2. Michael-type Friedel–Crafts reactions of indole and derivatives with  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>[a]</sup>

	R <sup>1</sup>	+ 0 R <sup>2</sup> R <sup>3</sup>	5 mol% <b>1a</b> H <sub>2</sub> O or H <sub>2</sub> O/THF (4:1), RT	$\mathcal{F}^{R^3}$	
Entry	Michael donor	Michael acceptor	Product	<i>T</i> [h]	Yield [%] <sup>[b]</sup>
1 <sup>[c,d]</sup>	<b>E</b>	o N	NH NH	1	96
2 <sup>[c,d]</sup>	Br	° N	Br. No	1	89
3 <sup>[c]</sup>	Z Z H	©_↓	C C C C C C C C C C C C C C C C C C C	0.5	90
4 <sup>[c]</sup>		° ≫	O T T T	0.5	85
5 <sup>[c]</sup>	N,	o L	CT N O	0.5	88
6 <sup>[d]</sup>	NH NH	°,	CT <sub>E</sub>	2	91
7	Br	°,	Br	4	81
8	N N N N N N N N N N N N N N N N N N N	°,	C C C C C C C C C C C C C C C C C C C	2	86
9	THE REPORT	°,	C N H	3	82
10	N.	°,	O N	3	80
11 <sup>[e]</sup>			Ph Ph Ph O Ph	48	78
12 <sup>[d]</sup>		NO <sub>2</sub>	Ph NO <sub>2</sub>	48	76
13 <sup>[c]</sup>	NH H	() f°	CT_N NH	48	72

esters, aldehydes, and nitriles were found to be less appropriate for Michael reaction with indole using the same catalytic system.

Cyclic enones, such as 2-cyclopentenone and 2-cyclohexenone, are generally less reactive than acyclic enones. Therefore they tend to proceed sluggishly, affording low yields even under prolonged reaction times.[5d] Catalyst 1a was demonstrated to be effective in promoting of the F-C reaction of indole with 2-cyclopentenone. The reaction proceeded smoothly to give the desired monoindolyl cyclopentanone in a moderate yield of 72% (Table 2, entry 13). A complication was observed when 2-cyclohexenone was employed as the Michael acceptor, giving triindolylcyclohexane as the major product (Table 2, entry 14). It is prone to overreact with indole under acidic conditions, making it difficult to obtain a monosubstituted product with satisfactory yield. The regioselectivity was affected owing to the competition between 1,4-addition and 1,2-addition of the indole to 2-cyclohexenone.<sup>[15]</sup> The difference in the formation of major product when using 2-cyclohexenone and 2-cyclopentenone as acceptors is accounted for by a torsional strain effect of their corresponding monoindolyl products.<sup>[16]</sup> Nevertheless, the replacement of indole with 2methylindole gave an increased regioselectivity in the Michael addition to 2-cyclohexenone. The corresponding 1,4-conjugated monoindoyl adduct was obtained as the major product in a moderate yield of 67% (Table 2, entry 15).

To validate the reusability of **1a**, 5 mol% catalyst was initially employed in the F-C reaction of indole (0.2 mmol) with MVK (0.4 mmol) in water (1 mL) for 1 h at room temperature. After

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Table 2. (Continued)



[a] Unless specified, Michael donor (0.20 mmol) was reacted with Michael acceptor (0.22 mmol) in  $H_2O/THF$  (0.8 mL/0.2 mL) at room temperature in the presence of **1a** (5 mol%). [b] Yields of isolated product after purification.[c] MVK (0.40 mmol) was used. [d]  $H_2O$  (1 mL) was used. [e]  $H_2O/THF$  (0.5 mL/0.5 mL) was used. [f] Conversion yield calculated based on indole.

recovery through a simple filtration and removal of volatile solvents under vacuum, the catalyst was reused in catalyzing the same model reaction without further activation. The reaction proceeded smoothly even after five runs, without any extension of reaction time or marked loss in yield (Figure 1). These positive results indicated that the sulfonated carbon-based solid acid **1a** could be recycled up to five times with no noticeable loss in its catalytic efficiency.



Figure 1. Catalytic performance of recovered **1a** in the F-C reaction of indole with MVK.

In conclusion, we have explored the efficiency of a carbon-based solid acid in catalyzing F-C reactions of indole and its derivatives with a variety of  $\alpha,\beta$ -unsaturated carbonyl compounds in water or H<sub>2</sub>O/THF solvents at ambient temperature. It is worthy to highlight the water-tolerant property of the carbon-based solid acid since it is capable of exhibiting a consistent high catalytic activity without being poisoned by water.<sup>[14]</sup> Furthermore, the solid acid, derived from D-glucose, which is accessible from nature in abundance, is considerably inexpensive. Most importantly, easy recovery of the catalyst upon completion of the reaction is achievable by simple filtration, and the recovered catalyst is

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reusable up to five times without any significant loss in catalytic performance. Thus, this carbon-based solid acid catalytic system serves as an environmentally benign tool for the efficient synthesis of 3-substituted indole derivatives.

### **Experimental Section**

All reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise stated. Methyl vinyl ketone, 2-cyclopentenone, and 2-cyclohexenone were distilled prior to use. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished

using silica gel 60 (0.010-0.063 nm). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using a base solution of potassium permanganate. Technical-grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded at room temperature on 300 MHz Bruker ACF 300 and 400 MHz Bruker DPX 400 spectrometers. The residual solvent signals were taken as the reference (7.26 ppm for <sup>1</sup>H NMR spectra and 77.0 ppm for <sup>13</sup>C NMR spectra in CDCl<sub>3</sub>). Chemical shift ( $\delta$ ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s=singlet, d=doublet, t=triplet, m=multiplet or unresolved. HR-MS (ESI) spectra were recorded on a Waters Q-Tof premier<sup>TM</sup> mass spectrometer. Elemental analysis was measured on a Perkin-Elmer Series II CHNS/O Analyzer 2400. Powder X-ray diffraction (XRD) was collected from a Shimadzu 6000 diffractometer. Carbonization of D-glucose was carried out on a Carbolite 1200°C three-zone tube furnace.

Typical procedure for Michael-type Friedel-Crafts reaction of indoles with  $\alpha,\beta$ -unsaturated carbonyl compounds: To a stirred mixture of indole (23.4 mg, 0.20 mmol) and 1a (29.0 mg, 0.01 mmol) in H<sub>2</sub>O (1 mL) or H<sub>2</sub>O/THF (0.8 mL/0.2 mL), the Michael acceptor (0.22 mmol) was added in one portion. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate (2 mL), filtered, and washed successively with water (5 mL), ethyl acetate (3× 5 mL), and diethyl ether (5 mL). The filtrate was collected and the organic layer was separated. The aqueous layer was extracted with ethyl acetate  $(3 \times 5 \text{ mL})$ . The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford the crude product, which was purified by column chromatography on silica gel to give the corresponding product. The remaining solid acid catalyst was dried under reduced pressure to remove all the volatile components, and then reused in the next run.

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