Sulfonic Acid-Functionalized (Bio)Materials as Catalysts for Efficient Amide Bond Synthesis

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Sulfonic acid carbon-(bio)based and natural clays-based catalysts were prepared and investigated for the first time as heterogeneous catalysts for amide bond synthesis by a Ritter reaction. The different SO3H-catalysts were screened using benzyl alcohol and acetonitrile as model substrates, and MWCNT-CSP revealed to be an efficient catalyst, affording the amide in 75% yield. The practical utility of the catalysts was demonstrated by a diverse range of amides, obtained from alcohols and nitriles, in moderate to good yields. Biomass derived platform alcohols, such as 5-HMF and furfuryl alcohol, were also tested as potential building blocks for the synthesis of biopolymers. The SO3H-catalysts revealed to be a highly efficient and environmentally friendly alternative to the conventional acid catalysts commonly used in the Ritter reaction.

Introduction

Amides are a functional group of paramount importance in both medicinal and organic chemistry.[1,2] The amide bond is the key chemical connection of proteins, and constitute the basis of the most versatile and extensively used synthetic polymers. In addition, compounds containing an amide bond are reported to possess several biological properties and are used for the treatment of many diseases such as the hypertension and management of edema, lung cancer and leukemia.[3,4] Due to their very attractive properties, such as high polarity, stability and conformational diversity, amides are one of the most popular and reliable functional groups in many areas of chemistry.[5]

The conventional method for amide bond formation involves activation of a carboxylic acid by an activating group, followed by nucleophilic displacement by a free amine. Although highly used, this method leads to the production of considerable amounts of waste.

Alternative methods to prepare amides have been developed, such as the Schmidt reaction (Scheme 1A), in which carbonyl derivatives react with an azide, under acidic conditions.[6,7] Other classical methods also include the Schotten-Baumann reaction (Scheme 1B), that consists on the reaction of an acid chloride with a primary or secondary amine under basic conditions;[8] and the Ugi reaction, a multi-

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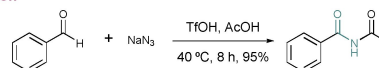*4169-007 Porto (Portugal)*
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Scheme 1. Methods for amide bond synthesis.[7–9,11]

component reaction requiring an aldehyde, carboxylic acid, isonitrile and amine (Scheme 1C).[9]

Among the various methods, the Ritter reaction is a highly attractive method to prepare amides (Scheme 1D), being particularly useful for the preparation of bulky amides, valuable precursors of hindered amines.[10]

The Ritter reaction consists of the reaction of a nitrile with an alcohol or olefin in the presence of a strong acid (usually sulfuric acid), hampering its application to compounds containing acid-sensitive groups. Over the last years, catalytic versions of the reaction have been developed (such as using 4-dinitrobenzenesulfonic acid – DNBSA, Scheme 1D).[10,11]

Heterogeneous catalysts have been evaluated in the production of nitrogen-containing molecules from different oxygen-containing feedstocks[12] including biomass resources.[13] Particularly, there are some examples of the use of heterogenous catalysts in Ritter reactions of alcohols including P_2O_5/SiO_2,[14] zeolites,[15–17] and, $HClO_4$-functionalized silica-coated magnetic nanoparticles (γ-$Fe_2O_3/SiO_2/HClO_4$).[18] Indeed, heterogeneous catalysts have emerged has a sustainable alternative to the homogeneous, offering several advantages, ranging from high surface area/nanosize to their rapid separation and recovery, while maintaining their selectivity in chemical reactions. Sulfonic acid functionalized catalysts have been widely used in sustainable catalysis and biomass valorization to biofuels and bioproducts. Peixoto *et al.* have developed new sulfonic acid-(nano)materials based on natural clays,[19,20] multi-walled carbon nanotubes (MWCNTs)[21] and bio-based carbons[22] (prepared from vineyard pruning waste). The catalysts have been used in biodiesel production,[19,20] Prins-Ritter reaction for selective synthesis of terpenoid-derived 4-amidotetrahydropyran compounds,[21,23] and production of fuel bioadditives as ethyl levulinate[20] and 5-(*t*-butoxymethyl)furfural[24] (continuous flow) from 5-hydroxymethylfurfural. Due to the excellent performance of these sulfonic acid catalysts under homogeneous conditions in the above mentioned reactions, we decided to expand our studies for the production of amides via the Ritter reaction using several substrates including the derived platform molecules, such as 5-HMF and furfuryl alcohol.

Herein, we disclose, for the first time, the use of sulfonic acid-based catalysts obtained by organosilylation with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) or sulfonation (using chlorosulfonic acid) of K10 and CLOI (montmorillonite), HNTs (halloysite nanotubes), MWCNTs (multiwalled carbon nanotubes) and Biochar (BIO, prepared from vineyard pruning waste), and its application as a sustainable alternative to amides production via the Ritter reaction.

Results and Discussion

The catalysts were previously characterized from different Techniques,[21–23] and the main physical-chemical properties are presented in SI, Table S1 (adapted[25]). The catalysts K10-CSP and MWCNTs-CSP present the highest specific surface area (S_{BET}), 155 and 181 m²/g, respectively. The -CSP functionalization introduced similar acid density to the K10, HNT, CLOI and BIO in

the following order: K10-CSP (0.80) ~ HNT-CSP (0.82) < CLOI-CSP (0.88) < BIO-CSP (0.98), although for the MWCNT-CSP catalyst the acidity introduced is lower than the observed for other catalysts, 0.40 mmol H^+/g. On the other hand the functionalization of aluminosilicates materials (natural clays) with -CSA allowed to obtain materials with higher acidity (mmol H^+/g), such as: K10-CSA (5.84) > HNT-CSA (2.23) > CLOI-CSA (1.78). In general -CSA functionalization allowed obtaining catalysts with higher acidity than the -CSP functionalization.

The catalytic studies were initiated with a screening of as-prepared nano-catalysts, and their efficiency was compared with *p*-TSA (*para*-toluenosulfonic acid) (Table 1). 1-Phenylethanol **1a** and acetonitrile **2a** were chosen as model substrates. First experiments were carried with **1a** (0.33 mmol) and **2a** (17.23 mmol) for 24 h under 100°C (Table 1), and different catalysts were investigated.

All catalysts afforded amide **3a** in moderate to good yields. Higher conversions were observed for catalysts bearing a *p*-toluenesulfonic group (CSP) anchored to the catalyst surface (Table 1, entries 2, 4, 6 and 8), which are the catalysts that present lower acid density (Table S1) comparing with the catalysts functionalized with -CSA (functionalization with chlor-

Table 1. Optimization of reaction conditions with different heterogeneous catalysts.[a]

Entry	Catalyst	Yield [mol %]
1	K10-CSA	34
2	K10-CSP	37
3	BIO-CSA	52
4	BIO-CSP	58
5	CLOI-CSA	54
6	CLOI-CSP	56
7	HNT-CSA	41
8	HNT-CSP	49
9	MWCNT-CSP	75
10[b]	*p*-TSA·H_2O	73

Reaction condition: [a] 1-phenylethanol **1a** (0.33 mmol), acetonitrile (17.23 mmol) and catalyst (50 mg), for 24 h under 100°C, [b] 1-phenylethanol **1a** (0.33 mmol), acetonitrile (17.23 mmol) and *p*-TSA·H_2O (10 mol%), for 24 h under 100°C.

Table 2. Effect of additives in the polymerization of furfuryl alcohol.[a]

Entry	Additive [%w/w]	Polymer [%][b]
1	BHT (1)	11
2	ChCl (1)	11
3	$Na_2S_2O_4$ (1)	4
4	$Na_2S_2O_4$ (5)	0.5
5	$Na_2S_2O_4$ (10)	5
6	No additive	100

Reaction condition: [a] Furfuryl alcohol (1.3 mmol), acetonitrile (68.92 mmol), *p*-TSA.H_2O (10 mol%) and additive (% w/w); [b] Relative %.

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doi.org/10.1002/cctc.202201318

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osulfonic acid). MWCNT-CSP showed to be the best catalyst leading to amide **3a** with 75% yield (Table 1, entry 9) and curiously this is the catalyst with lower acid density and higher surface area. These results demonstrate that, in this Ritter reaction, moderate H^+ acidity combined with a high surface area (181 m²/g) are desirable properties to reach higher yields of **3a**. A comparison study was performed, using *para*-toluenesulfonic acid monohydrated as catalyst, achieving the target molecule with a yield of 73%, which is slightly lower than that of MWCNT-CSP, (Table 1, entry 10).

From the results it is possible to notice that carbon based catalysts are the most efficient, rendering yields higher than 50%, independently of the functionalization, which is in accordance with the recently published results on the Prins-Ritter reaction of (−)-isopulegol with benzaldehyde and acetonitrile.[25] A curious fact transversal to all experiments, was the dimerization of **1a**, to bis(1-phenylethyl)ether **4**. The formation of this side product was reported in a Ritter reaction catalyzed by FeCl₃.[26] The recyclability of MWCNT-CSP as catalyst was investigated. After the first cycle, the catalyst was recovered by centrifugation and washed twice with acetonitrile, HCl (1 M, in order to activate the sulfonyl groups) and methanol. Next, a new reaction was run again with the recovered catalyst, giving the target product in a decreased yield of 42%. The catalyst deactivation and consequent yield reduction can be attributed to partial cleavage of attached sulfonic groups from MWCNT matrix,[27] or to deposition of organic matter on the catalyst surface. To assess the extent of catalyst deactivation, the TG and XPS spectrum analysis of the used catalyst washed with CH₃CN/HCl/MeOH were compared with the ones of the catalyst washed with CH₃CN and MeOH (Figure 1 and S1 in SI, respectively). As it is possible to see the TG of the catalyst washed in absence of HCl (Figure 1) revealed higher weight loss at temperatures around 200–300 °C, which is indicative of organic moieties deposited on the catalyst surface. This weight loss was not observed when the used catalyst was washed with HCl, presenting a TG similar to the fresh catalyst suggesting that this acidic washin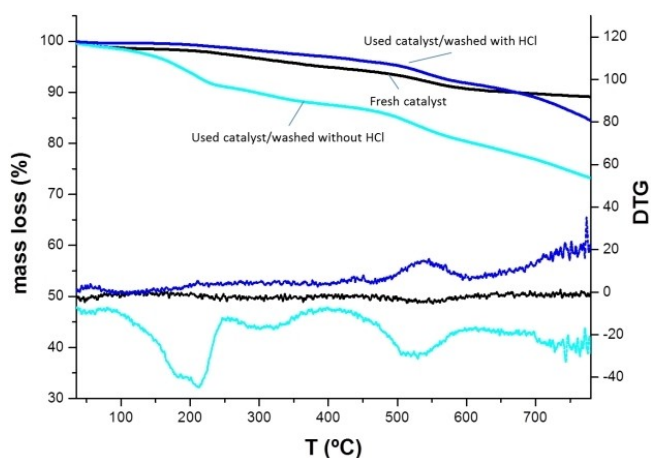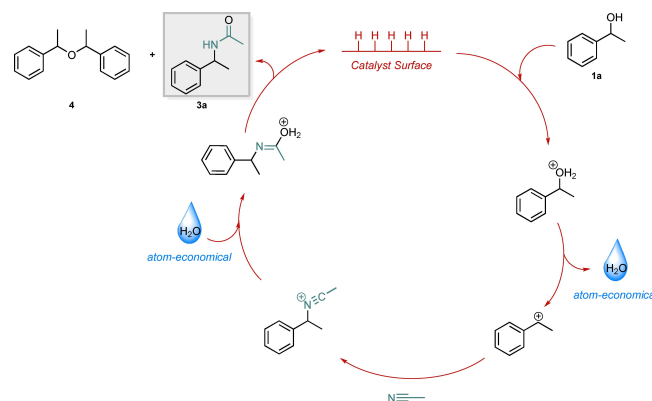g treatment removes the organics from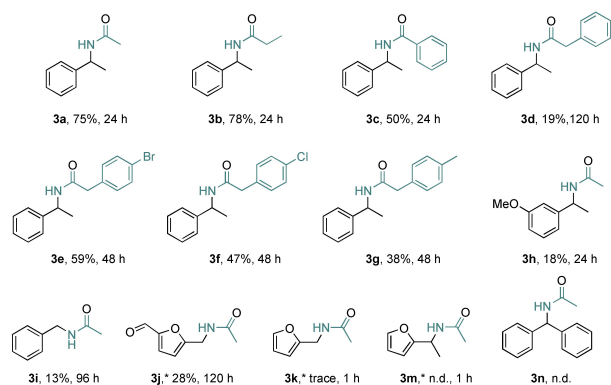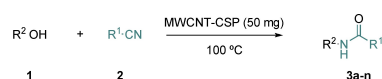 the catalyst surface. Both, fresh and used, MWCNT-CSP catalysts, led to a weight loss in the range of 400–600 °C attributed to the decomposition of the organic chain of the organosilanes covalently linked, demonstrating that the sulfonic acid functional groups are still covalently linked to the matrix after washing, independently of the use or not of HCl. This is also corroborated by the XPS analysis. By the S 2*p* high resolution spectra it is possible to observe two peaks at 168.4–168.9 eV and 169.6–170.1 eV, ascribed to the S 2$p_{3/2}$ and S 2$p_{1/2}$ components, respectively, split by 1.2 eV, corresponding to sulfur in its oxidized form in an −SO₃ environment, proving the presence of SO₃H species in the used catalysts. However, the S content of the fresh catalyst, by XPS analysis, was 0.15 mmol/g_{cat} and for the used catalyst, washed with or without HCl, was 0.06 and 0.13 mmol/g respectively. Thus, washing the used catalyst with HCl not only promotes the elimination of the organic compounds deposited in the catalyst surface, but also favors sulfonic acid leaching and a consequent reduction of the catalyst activity in the consecutive catalytic cycles.

According to the accepted mechanism for the classical Ritter reaction, this reaction follows the mechanism depicted in Scheme 2. First, **1a** is protonated by the acid, releasing a water molecule with the consequent formation of the carbocation, which is trapped by the nitrile. Next, hydrolysis of the nitrilium specie leads to the amide bond formation – compound **3a**. As mentioned before, we have also observed the formation of bis(1-phenylethyl)ether (**4**), generated from the reaction of **1a** with the carbocation.

Subsequently, the catalytic activity of MWCNT-CSP was explored with different alcohols and nitriles using the optimized conditions to achieve the corresponding amide (Table 1, entry 9). It was found that the Ritter reaction proceeded and gave the desired product in moderate to very good yields (Scheme 3). When secondary benzyl alcohol was used, amide **3a** was produced in very good yield, 75%. On the other hand, when a primary benzyl alcohol is used, the yield decreased to 13% (**3i**), as expected due to the lower reactivity of primary alcohols according to the Ritter reaction mechanism. When a secondary alcohol bearing a *m*-methoxy group **3h** was used, a remarkable decrease in yield was observed (18%). 1,1-Diphenylmethanol **3n** was also tested but the presence of the amide

Figure 1. TGA curves (N₂ flow) of the fresh catalyst (MWCNT-CSP) and the used catalyst washed with HCl and without HCl.

Scheme 2. Proposed mechanism of Ritter reaction with different catalysts.

Scheme 3. Scope of the Ritter reaction with MWCNT-CSP catalyst.

Figure 2. ^{13}C CP MAS NMR spectrum of humins.

was not detected, probably due to steric effects between the catalyst and the alcohol. The reactivity of 5-HMF **1 j**, a biomass derived compound was also investigated. During our study, we observed the formation of a dark-brown solid leading to low yields. In literature this behavior was also reported, leading to the formation of a polymer material as a side product.[28] In order to avoid formation of this polymer, different additives were tested, and the best was $Na_2S_2O_4$ (1% w/w). When the reaction was carried out in the presence of this additive, the corresponding amide was achieved in 28% yield (**3 j**), along with the polymer, however in a much lower amount. Other biomass derived alcohols were tested, such as furfuryl alcohol. Unfortunately, the polymerization was observed and consequently there was no formation of the corresponding amide **3 k**. Subsequently, this polymer was analyzed by Magic-Angle Spinning (MAS) solid state (ss) NMR.

The ^{13}C CP MAS NMR spectrum of the obtained polymer reveals an overall pattern compatible with the presence of polyfurfuryl alcohol (PFA) in accordance to previously reported spectra.[29] Using ^{13}C NMR, ATR-FTIR, Raman and DFT analysis, Tondi *et al.* concluded that PFA was mainly constituted by linear unconjugated polymers, with some furanic units undergoing Diels-Alder rearrangements and γ-lactone arrangements in the terminal moieties.[29] The current spectrum reveals the predominance of a linear furanic polymer, where the unsaturated carbons resonate at 153 and 110 ppm, and the methylene carbons at 29 ppm (Figure 2). A broad signal at 38 ppm can be assigned to the presence of Diels-Alder arrangements and/or methylene bridging structures. Minor contributions to the magnetization can be attributed to the presence of diketones with the carbonyl carbon signals at 206 ppm.

The humins formation was investigated with furfuryl alcohol and acetonitrile under acidic conditions, with different additives (Table 2 and Table S2). It was found that the polymer formation was slightly suppressed in presence of butylhydroxytoluene (BHT) and choline chloride (ChCl) in 1% w/w (Table 2, entries 1
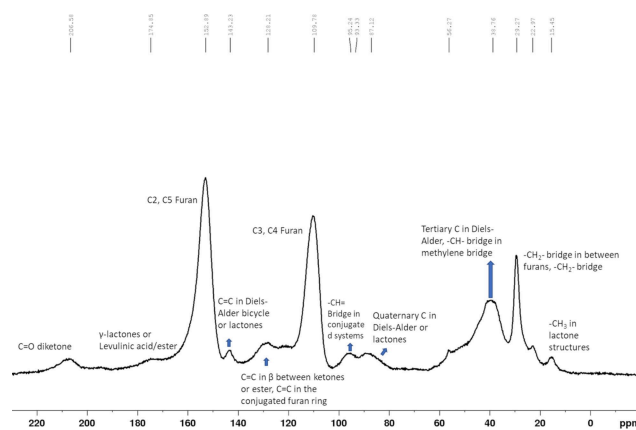
and 2). In contrast, with the same quantity of sodium dithionite ($Na_2S_2O_4$), this side product decline substantially (Table 2, entry 3). Following the success of this additive, different concentrations have been carried out. In presence of 5% w/w (Table 2, entry 4), a significant effect was observed in the stability of furfuryl alcohol leading to a low conversion rate to the polymer. However, when the concentration of this additive was 10% w/w, the formation of the polymer increased (Table 2, entry 5). In the same way, 1-(2-furfuryl)ethanol (Scheme 3, 3m) revealed the polymerization of the starting material, and a study with the presence of $Na_2S_2O_4$ (1% w/w) was performed. Fortunately, polymerization was not observed, but there was not formation of the corresponding amide.

Conclusion

We describe the synthesis of amides using diverse heterogeneous catalysts namely, K10, BIO, CLOI, HNT and MWCNT, as sustainable alternatives to the stoichiometric amounts of strong acids, commonly associated with the traditional Ritter conditions. Among the various sulfonic acid carbon-(bio)based and natural clays-based catalysts, MWCNT-CSP revealed to be the most efficient catalyst. Reusability tests were performed and some loss of activity was observed after washing with CH_3CN/HCl/MeOH. This washing contributes to remove organics adsorbed to the surface although it also contributed to some $-SO_3H$ leaching, resulting in a loss of activity. Recovery tests are being performed to improve the catalyst stability during the recycling tests. This efficient catalytic protocol allows access to a wide range of amides, including amides derived from the challenging furfuryl alcohol. The easy preparation of the catalyst, simplicity of the protocol and separation of the catalyst from the product, makes this route very attractive for the transformation of inexpensive raw materials to high-value amides, using biomass-derived catalysts.

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doi.org/10.1002/cctc.202201318

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Experimental Section

Materials and methods

The experimental part of this article involved the use of general laboratory procedures. Reagents and solvents used are commercially available, specifically Carlo Erba, LabChem, Alfa Aesar, BDH Chemicals, Honeywell and Sigma Aldrich. It was not necessary an additional step of purification. Reactions were followed by Thin-Layer-Chromatography (TLC) using Macherey-Nagel silica gel 60 F254 aluminium sheets with 0.2 mm of layer thickness. TLCs were revealed under UV lamp at 254 nm, and subsequently by phosphomolybdic acid solution by Sigma Aldrich for the detection of some alcohol derivatives and amides formation. For purification, column chromatography was performed using Carlo Erba 60 A silica gel (40–63 μ) with respective eluent for each reaction. Preparative Thin-Layer Chromatography (PTLC) was performed using Merk Kieselgel 60 F254 silica gel supported on a 0.5 mm glass surface.

^{1}H NMR and ^{13}C NMR spectra were measured at 400 and 101 MHz, respectively, with Bruker ARX 400 or Bruker Avance III 400 spectrometers. The samples were prepared on 5 mm tubes using $CDCl_3$ as solvent, and the corresponding solvent residual peaks as reference signal. Chemical shifts (δ) for NMR spectra were expressed in part per million (ppm) units.

Solid state ^{13}C MAS NMR spectrum was acquired in a 11.7 T (500 MHz) AVANCE III Bruker spectrometer operating at 125 MHz (^{13}C), equipped with a BBO probehead. The samples were spun at the magic angle at a frequency of 5 kHz, using 4 mm diameter rotors at room temperature. The ^{13}C MAS NMR experiment was acquired with proton cross polarization and total suppression of sidebands (CP-TOSS), with a contact time of 2.0 ms, a recycle delay of 5.0 s and a sweep width of 37 kHz. Data processing was performed with Topspin 4.1.4 (Bruker).

Thin Layer Chromatography (TLC) was performed on Merck Kieselgel GF 254 0.2 mm plates. Melting points were measured using Reichert Thermovar melting point apparatus, equipped with a Kofler plate. IR-ATR spectra were acquired between 4000–400 cm^{-1} using a Perkin-Elmer Spectrum Two spectrometer equipped with an attenuated total reflectance module. Low resolution ESI mass spectra were carried on an ion trap mass analyser (Thermo Scientific LCQ Fleet Ion Trap LC/MS) equipped with an electrospray interface.

Thermogravimetric analysis (TGA) was carried out using a Hitachi STA7200RV Instruments; ca. 10 mg of sample were loaded into an alumina microcrucible and heated to 800 °C at 10 °C·min^{-1} in flowing N_2.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra HSA, coupled with VISION software for data acquisition, at Centro de Materiais da Universidade do Porto (CEMUP), Porto, Portugal. The equipment used a monochromatic Al Kα X-ray source (1486.7 eV); operation conditions: 15 kV (90 W); Fixed Analyser Transmission (FAT) mode; 40 eV (regions ROI) and 80 eV (survey) of pass energy.

General Procedure for catalysts preparation

All the sulfonic acid-catalysts were prepared according to the procedures described by Peixoto et al.[19–22] Reagents: Montmorillonite K10 (K10), halloysite nanotubes (HNT), p-toluenesulfonic acid monohydrate (≥98%) were purchased from Sigma Aldrich, chlorosulfonic acid (≥98%) from Fluka; 2-(4-chlorosulphonylphenyl)ethyltrimethoxysilane (CSPTMS, 50% in methylene chloride) from ABCR GmbH; Cloisite-Na$^+$ (CLOI) was

kindly provided by Southern Clay. Multi-walled carbon nanotubes (MWCNT) were commercially obtained from Nanocyl S.A. (>95% carbon purity). Unless stated otherwise, all reagents were used without further purification.

The −SO_3H functionalization and characterization of halloysite nanotubes (HNTs), CLOI-Na+ and K10 clays via organosilylation and sulfonation with chlorosulfonic acid (ClSO$_3$H) have been reported in our previous publication.[19,20]

The MWCNT functionalization was performed according to Peixoto et al.[21] in the previously oxidized multi-walled carbon nanotubes (o-MWCNTs); MWCNT-CSP: 3.0 g of o-MWCNT were suspended in 200 mL of dry toluene and CSPTMS (1.38 mL). The mixture was refluxed for 24 h under inert atmosphere. The final solid (MWCNT-CSP) were isolated by filtration washed and dried at 110 °C overnight.

BIO-CSA and BIO-CSP functionalization were performed according to Peixoto and co-workers[22] using biochar material obtained by hydrothermal carbonization of vineyard pruning wastes in water at 250 °C. BIO-CSA: 1 g of biochar was suspended in 30 mL of $CHCl_3$ using a 50 mL round-bottom flask. The suspension was maintained under magnetic stirring for dropwise addition of 1 mL of ClSO$_3$H. The solution was kept at 65 °C for 2 h. BIO-CSP: 2 g of biochar was dispersed in anhydrous toluene (100 mL). The addition of CSPTMS (1.84 mL; 7.8 mmol) was carried out and the reaction was maintained at 120 °C, under magnetic stirring and inert atmosphere for 24 h. After washing, the catalysts BIO-CSA and BIO-CSP was dried under 100 °C.

General procedure for the synthesis of N-(1-phenylethyl)acetamide (3 a) with different catalysts

A Schlenk tube was equipped with a stirred magnetic bar. Subsequently was charged with the 1-phenylethanol **1 a** (40 μL, 0.33 mmol), acetonitrile (1 mL, 19.15 mmol) and the catalyst (50 mg), and sealed with a subaseal. The reaction mixture was stirred at 100 °C in an oil bath. After reaction completion, the mixture was transfer to a falcon and washed twice with acetonitrile, chloride acid sat. (1 M), methanol, and centrifuged (5 min, 2400 rpm). The supernatant was filtered and evaporated. The products were extracted with ethyl acetate (3×20 mL), dried over Na_2SO_4, and evaporated to dryness. The resulting product was purified by preparative thin layer chromatography with 2:1 of ethyl acetate:hexane (results indicated in Table 1).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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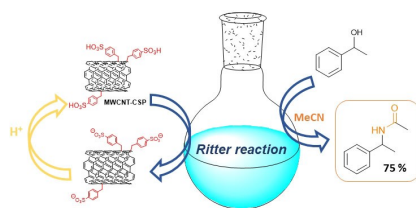
RESEARCH ARTICLE

Ritter reaction: Amide bond synthesis catalysed by MWCNT-CSP. This efficient catalytic protocol allows access to a wide range of amides, including amides derived from the challenging furfuryl alcohol. From in-expensive raw materials to high-value amides.

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Sulfonic Acid-Functionalized (Bio)Materials as Catalysts for Efficient Amide Bond Synthesis