Review

Chronicle of Nanocelluloses (NCs) for Catalytic Applications: Key Advances

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Abstract: Nanocellulose (NC) is a biomaterial with growing interest in the field of nanocomposites and sustainable materials. NC has various applications including biodegradable materials, reinforcing agents, packaging films, transpiring membranes and medical devices. Among the many applications, the use of NC functionalized with organic and inorganic groups has found wide use as a catalyst in chemical transformations. The goal of this review is to collect the current knowledge on its catalytic applications for chemical groups conversion. We have chosen to organize the manuscript according to subdivision of NC into Bacterial Nanocellulose (BNC), Cellulose Nanocrystals (CNCs), and Cellulose Nanofibers (CNFs) and their role as inorganic- and organic-functionalized NC-catalysts in organic synthesis. However, in consideration of the fact that the literature on this field is very extensive, we have decided to focus our attention on the scientific productions of the last five years.

Keywords: bacterial nanocellulose (BNC); cellulose nanocrystals (CNC); cellulose nanofibrils (CNFs); nanocellulose functionalization; nanocellulose synthesis; catalytic nanocellulose applications

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1. Introduction

Cellulose is the main component of lignocellulosic biomasses, with an average percentage of 40–50 of the total weight. It is the most abundant polysaccharide on Earth, with an estimated annual production of 7.5×10^{10} tons [1,2]. From a chemical point of view, it is composed of β -D-glucopyranoses (ca. 5000 and 10,000 units), linked by β -1,4-glycosidic bonds. β -Glycosidic bonds force the entire structure of the polysaccharide to a linear arrangement, due to the pyranose chair conformation and the equatorial disposition of the substituents within the subunits, that corresponds to a minimum of energy of the entire structure [3].

Due to the extensive potential applications of this inexhaustible material [4,5], nanocelluloses (NCs) became in brief time one of the main topics of research worldwide. In particular, NCs have shown excellent properties like strength, high Young's modulus, biocompatibility, tunable self-assembly, and thixotropic behavior, becoming groundbreaking in plenty of fields like optoelectronics, antibacterial coatings, packaging, engineered polymer composites, medicine (tissue scaffolds, drug delivery, biosensors, etc.), energy storage, catalysis, and environmental remediation [6,7]. Very often the nanocellulose (NC) is subjected to functional modifications through chemical reactions. These modifications are frequently performed to improve the characteristics and performance of nanocellulose-based materials and more specifically to obtain nanocellulose derivatives with enhanced lipophilic characteristics through acetylation, benzylation or alkylation and with increased hydrophilic features by sulfonation or oxidation reactions. At the same time, it is necessary to preserve the structural integrity of modified nanocellulose to ensure its stability during the use as heterogeneous catalyst in organic transformations. Moreover, the almost always

superficial modifications ensure the excellent catalytic performance and the maintenance of its intimate structure for an easy recovery and a possible reuse of the catalyst.

Despite the always growing number of studies about the preparation and their applicative evaluation, NC materials can be classified into just three main nanoforms: bacterial nanocellulose (BNC), cellulose nanocrystals (CNCs), and cellulose nanofibers (CNFs). The parameters which define the classification of these materials are mainly related to the methods of preparation (biological, chemical, and mechanical), the morphological attributes, and the crystallinity degree of the material; for a deeper point of view on the physical properties of NCs, the reader can refer to [8].

In spite of a lot of works have been published about the preparation, the chemical transformation and the general employ of this nanomaterials, to our knowledge literature reports only two papers which examine the role of nanoparticles (NPs)-decorated NC-derivatives as inorganic catalysts [9,10]. On the other hand, the catalytic application of organic-functionalized NCs still have not been properly reviewed. For these reasons, the goal of this work is to provide a complete review on the role of inorganic- and organic-functionalized NC-derivatives in organic synthesis with a particular emphasis on the last five years.

2. Bacterial Nanocellulose

Bacterial nanocellulose (BNC), also defined bacterial cellulose (BC), is an exceptional natural polymer with a great variety of technical applications. BNC was firstly described in a scientific paper by A.J. Brown in 1886, as produced by *Bacterium aceti* through fermentative processes to produce nanoscale cellulose [11]. Cellulose nanofibers can be also produced, as extracellular secretion, by several species of bacteria, such as *Aerobacter*, *Acetobacter*, *Agrobacterium*, *Azotobacter*, *Rhizobium*, and *Pseudomonas* [12,13]. *Acetobacter xylinus*, also known as *Gluconacetobacter* or *Komagataeibacter xylinus*, a non-pathogenic Gram-negative aerobic bacteria, is considered the most efficient cellulose producer, and the most extensively studied [12]. BNC has the same molecular formula as plant cellulose but is characterized by a 3D porous network structure with unique features. First of all, it has high purity since it is hemicellulose- and lignin-free, with a high water content of 99% and hydrophilicity [13]. It possesses high crystallinity (up to 80%) with a resulting high thermal stability and a high degree of polymerization (up to 20,000). Finally, BNC exhibits high flexibility, with a value of 118 GPa for Young's modulus of single nanofiber, which is comparable to steel [14]. BNC nanofibers have a high aspect ratio around 20–100 nm in width and 1–9 μm length, with a surface area superior to that of plant cellulose [12]. BNC is very versatile since it can be obtained in different shapes and thicknesses, such as pellicle, disk, or aggregate. Finally, BNC is more environmentally friendly than its vegetal counterpart, due to its high purity, which does not require additional purification procedures. Moreover, the identification of different waste biomass as a useful carbon source for a prospective industrial BNC production, together with its considerable environmental biodegradability and biocompatibility make it an ecofriendly material. The BNC features are influenced by the fermentation conditions such as the carbon and nitrogen sources, the temperature, the incubation time, and agitation. Furthermore, it is possible to alter the BNC structure and the morphology by adding chemical reagents in the culture medium or the growing fibers, to give nanocomposite properties [15,16]. In this way it is possible to obtain a versatile template material for various applications, from medical devices to innovative materials with electrical properties [16,17].

Thanks to its numerous hydroxyl groups it could be chemically functionalized to give materials with enhanced chemical and physical properties. As an example, BNC oxidation enhances its biodegradability and solubility. Instead, esterification of the BNC could be a strategy for improving the capability of integration with other organic polymers, or for the delivery of active pharmaceutical ingredients [12].

Very attractive aerogels can be obtained from BNC, through freeze-drying processes. The resulting porous solid material can be used as a template for numerous catalysts in

diverse applications [12,18,19]. It is worth noting that these BNC aerogels also are the starting material in high-temperature pyrolysis processes under an inert atmosphere, to obtain carbon nanofibers with a 3D nanostructure [20]. Although numerous papers reported the use of these advantageous catalysts, this topic is out of scope for the present review, and only pristine BNC, suitably modified without pyrolysis processes will be examined.

Readers can find a complete survey about the advancements in bacterial cellulose applications in previous, very exhaustive reviews [9,21–26]. The most interesting bacterial cellulose applications as a catalyst from 2016 until the present, are reported herein.

2.1. Inorganic Functionalization of Bacterial Nanocellulose and Catalytic Applications

Many inorganic compounds, like metal oxides, metal sulfides, silica, or metal nanoparticles, have been integrated into BNC, exploiting its isotropic 3D nanostructure to obtain versatile heterogeneous catalysts. With the aim to prepare nanocomposites with enhanced activity, it is possible to add these inorganic materials through different synthetic strategies. Among them, three strategies have been most used and reported in the literature: (i) the mixing under simple agitation or ultrasound-assisted conditions; (ii) the absorption through solvothermal processes; and (iii) in situ incorporation in the growth medium. The catalytic applications of these new materials are classified in the following sections.

2.1.1. Catalytic Transformation of Organic Compounds for Environmental Purposes

Many efforts have been made in the last years for the treatment of industrial wastewater, to eliminate or limit the pollutants. For example, the textile industries contribute a lot to aquatic pollution with azoic dyes. The reduction of these contaminants in non- or less-toxic compounds was investigated, using transition metal-based nanoparticles, which are more economical than noble metal nanoparticles. Thiruvengadam and Vitta in 2017, proposed the use of BNC as flexible and multifunctional Ni-based nanocomposite to reduce methyl orange (MO) used as a model dye pollutant [27]. The authors obtained Nickel-Bacterial Cellulose (NiBNC) nanocomposite at different nickel concentration using the “inverse chemical reduction” technique. It consisted of the immersion of a BNC hydrogel firstly in a sodium borohydride (NaBH_4) solution and subsequently in a NiCl_2 solution. Finally, the resulting black colored NiBNC was hot-pressed at 70 °C and 4 MPa, to obtain a dried NiBNC sheet with a final formation of highly interconnected metal nanoparticles in a BNC network, with magnetic and electrical properties. The reduction catalytic activity was also tested, and the NiBNC was able to reduce the UV-absorption of a methyl orange solution if compared with pristine BNC. The reusability of this catalyst was checked, and the authors highlighted that a high efficiency was maintained if the catalyst was not stored in an aqueous solution between the cycles. Xu et al., in 2018, developed a novel flexible membrane for the water pollution treatment, based on BNC loaded with graphene oxide (GO) and palladium nanoparticles (Pd-NPs) [28]. At first, GO flakes were introduced as a uniform dispersion in the growing BNC nanofibers, allowing intercalation in a “layer by layer” manner. The resulting material showed more robustness of the pristine BNC, a crucial property for water treatment materials. After the formation and cleaning in alkaline solution, the GO/BNC hydrogel was cut in the desired measures and freeze-dried to give GO/BNC aerogel with a large specific surface area. To add Pd-NPs to the GO/BNC structure, it was immersed in a PdCl_2 solution, dried, and then washed with a NaBH_4 solution leading to in situ formations of Pd-NPs (Figure 1). The newly formed Pd/GO/BNC membrane showed a large loading of Pd-NPs in the final membrane and was used dried for the catalytic test, in which methyl orange dye-contaminated water, in presence of NaBH_4 , was filtered through it. The rate of methyl orange degradation was measured with a simple Pd/BNC membrane that was lower compared to that of Pd/GO/BNC membrane. Its powerful activity was highlighted testing this sheet as a filter for a cocktail solution of contaminants with a concentration of 10 mg L⁻¹: methylene blue 1 (MB), 4-nitrophenol 2 (4-NP), and rhodamine 6G 3 (R6G). In all cases, the colored solution became completely colorless after filtration through the Pd/GO/BNC membrane, probably due to the lamellar

structure of the membrane that assures an excellent interaction with the Pd-NPs for the reduction activity. It is worth noting that the entire membrane preparation procedure is easily scalable. This feature together with the high spread catalytic activity and the stability showed in the stress test, make this new material interesting for industrial application.

Figure 1. Schematic illustration of the steps involved in the fabrication of Pd/graphene oxide (GO)/bacterial nanocellulose (BNC) and its use.

Very recently, the research group of Kamal et al. proposed different examples in which BNC was used as a high surface area support for transition metal nanoparticles stabilized with carboxymethyl cellulose (CMC) like cobalt (CMC-Co-BNC) [29], copper (CMC-Cu-BNC) [30], and nickel (CMC-Ni-BNC) [31]. In these works, metal chloride and CMC (1 wt%) solutions were mixed, then hydrazine hydrate and ascorbic acid were slowly added. Microwave heating of the resulting solution led to the carboxymethyl cellulose-metal (CMC-M) nanoparticles. Finally, the CMC-M-BNC dip-catalyst was obtained by simple dropping and spread of the CMC-M suspension on the BNC sheets previously obtained by a *Gluconacetobacter xylinum* culture (Scheme 1).

Scheme 1. Preparation of the colloidal carboxymethyl cellulose (CMC)-M nanoparticles and carboxymethyl cellulose (CMC)-M-BNC dip-catalyst.

All these catalysts were tested on the reduction of methylene blue 1 (MB) and different nitrophenols: 4-nitrophenol 2 (2-NP), 2,6-dinitrophenol 4 (2,6-DNP), and 2-nitrophenol 5 (2-NP) with CMC-Co-BNC, CMC-Cu-BNC, and CMC-Ni-BNC, respectively. In all cases, the CMC-M-BNC catalyst was able to reduce the dye pollutants, both alone and in combination, even if the colloidal CMC-M was found to catalyze the reaction faster than the heterogeneous CMC-M-BNC. The reusability was also tested with good conversion results after four cycles. The easier separation procedure of the heterogeneous catalyst, compared to the colloidal one that requires long centrifugation times for its recovery, suggests that the supported CMC-M-BNC could be more useful for real applications.

The hypothesized reaction mechanism could explain the different reaction rates measured for the CMC-M and the CMC-M-BNC. Both the reducible molecules and the sodium borohydride move on the nanoparticle surface. The NaBH_4 transfers a hydride on the reducible molecule, while an electron was transferred from it to the catalyst. Then, the reduced molecules leave the catalyst surface and spread in the solution. By then, another reducible molecule could be adsorbed. The authors hypothesized that the anionic surface of the CMC favored a strong interaction with the reducible molecules. Consequently, a fast catalytic reaction occurs (Scheme 2).

Scheme 2. (a) Chemical reduction of nitrophenols (2, 4, 5) and methylene blue (1) by NaBH₄ using CMC-M or CMC-M-BNC; (b) reaction mechanism.

After simple oxidation of the pristine BNC, it is possible to highly improve the metal absorption capacity maintaining, at the same time the crystallinity and crystal size of the nanofibers [15]. In addition, BNC TEMPO-mediated oxidation has been combined, also with defibrillation to allow a higher metal nanoparticles inclusion capability. In 2017, Chen et al. exploited this option using the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation reaction to obtain a BNC with carboxyl groups on the glucose moieties (TOBNC) as support for Au nanoparticles (Au-TOBNC) [32]. Before the oxidation reaction, it was necessary to fibrillate BNC into a slurry, then the reaction proceeded by adding TEMPO, NaBr, and NaClO under mild aqueous conditions. The TOBNC as obtained was then mixed with a HAuCl₄ solution in presence of sodium borohydride to give the Au-TOBNC catalyst (Scheme 3).

Scheme 3. Synthetic procedure of AuNPs supported by TOBNCs.

The average particle size for AuNP-TOBNC was lower than the unsupported AuNPs, and it was probably due to the carboxyl groups, which in the dissociate form could immobilize tighter the AuNP, allowing a more uniform distribution of the particle size. The influence of the pH on the amount of AuNPs loaded was studied. When pH was 3.2–11.3 it was observed a changing color of the suspension reflecting the increase of the amount of AuNPs. It was probably due to the associate or dissociated form of the carboxyl groups. Then, the Au-TOBNC catalyst was tested for the reduction of 4-nitrophenol (4-NP) 2 by NaBH₄ as a reaction model. The reduction of 4-nitrophenol (4-NP) 2 to 4-aminophenol 6 (4-AP) proceed almost 20-fold faster than the AuNP without TOBNC support. Probably, because the TOBNC allowed a better Au exposure to the reagent when adsorbed on the single nanofiber, it was well dispersed. Finally, the influence of the temperature on the reduction reaction was evaluated, and the rate of substrate activation and the rate of product desorption achieved a balance almost at 65 °C. This work was very important because of the higher catalytic efficiency than the values reported before for analog catalyst [33].

2.1.2. Photocatalytic Applications of BNC-Inorganic Composites for Environmental Remediation

The advanced oxidation processes (AOPs) are another way for the water removal of dyes and pollutants, which were under investigation through heterogeneous catalysis in the last year. Thanks to its unique features, the BNC can be considered an excellent material substrate for the design of a potential Fenton-type catalyst. In 2018, Wibowo et al. synthesized a Fenton-BNC catalyst, by immersing a BNC hydrogel in FeCl_2 and FeCl_3 solutions at different concentrations, with a 1:2 molar ratio between Fe(II) and Fe(III) [34]. After one night, the hydrogel color changed from white to yellow and was immersed in a NaOH (4 M) solution to oxidize the metal, with a final black color for the hydrogel. Finally, the Fenton-BNC hydrogel was freeze-dried to give a Fenton-BNC aerogel that was used for the catalytic degradation studies of methylene blue (MB) 1, used as dye pollutant model. The authors demonstrated that the heterogeneous Fenton catalyst supported by BNC possessed better catalytic activity than the bare Fenton catalyst prepared without BNC. As a further advantage, Fenton-BNC could be easily recovered by using an external magnetic field thanks to its magnetic features.

Very recently, Hu and co-workers proposed a new efficient and recyclable photocatalyst based on TiO_2 , non-woven polypropylene (NWP), and BNC [35]. In particular, TiO_2 nanoparticles were loaded onto NWP, and this sample was placed in the culture medium of *Gluconacetobacter x.*, in order to fix the nanoparticles in the growing cellulose (Figure 2). The TiO_2 -NWPBNC was used for the MB degradation catalytic tests, confirming that TiO_2 was efficiently embedded into the composite film, maintaining a good degradation performance with an MB removal rate over 92% after 2 h of reaction. Furthermore, after 5 cycles less than 10% of removal rate reduction was measured, showing also good reusability.

Figure 2. Preparation process of TiO_2 -loaded NWPBNC composite film.

2.1.3. Electro-Catalytic Applications of Inorganic-Functionalized Bacterial Nanocellulose

As previously reported [9], BNC can be converted into a material with electrical properties by inorganic functionalization with suitable transition metals. In this work, the authors measured an increase of the room temperature electrical conductance for a flexible BNC sheet functionalized with a 20 vol% of Ni nanoparticles. It is worth noting that the NiBNC membrane could be useful both for biodegradable and bendable electronic devices thanks to its unique properties to conduct both in the hydrogel or dried state, respectively.

Zhou and co-workers in 2019, developed a CuO/Cu nanocomposite electrode supported on BNC as a catalyst for efficient CO_2 electrochemical reduction to CO [36]. This electrode was obtained by applying an in situ chemical reduction process, in which BNC sheets were immersed in a Cu(II) salt solution of ethanol and water. NaBH_4 was added as a reducing agent, together with an NaOH solution (0.1 M), and the mixture was heated at 30°C for 90 min. Different CuO/Cu -BNC membranes were obtained as a function of the NaBH_4 concentration after washing with deionized water. Electrochemical activity and performance tests were carried out and in particular, the $\text{CuO/Cu}_{4:3}$ -BNC prepared with a 0.3 M concentration in NaBH_4 (with a 4:3 molar ratio between $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaBH_4) was evaluated as an efficient catalyst for electrochemical CO_2 reduction. The $\text{CuO/Cu}_{4:3}$ -BNC catalyst showed high faradaic efficiency of 53% for CO formation at a low overpotential of 490 mV, for over 40 h. Furthermore, it was compared with a conventional

CuO/Cu composite catalyst supported on carbon paper and it was highlighted that an enhanced electro-catalytic performance was obtained due to its unique structural advantages, such as high surface area, optimal CuO/Cu composition that allowed a facilitating charge, and mass transport and ability to promote the conversion of CO₂.

2.1.4. Synthetic Applications of BNCs Grafted with Inorganic Catalysts

The use of a heterogeneous catalyst is in great demand, also in organic synthesis, and BNC responds with its peculiar features. In 2019, Jeremic et al. carried out an extensive study on the influence of the BNC production parameters and its use in transition metal nanocomposites for the catalysis of cross-coupling reactions [37]. Firstly, the authors studied the influence of the single parameters, such as pH, glucose concentration, and day of incubation, for the optimization of BNC production. In addition, for the first time, they successfully used a sugar mixture, a product of grass biomass treatment [38], as a carbon source for BNC production, obtaining the valorization of non-food renewable biomass as starting material. Then, the authors evaluated BNC application as solid supports for transition metals for the synthesis of heterogeneous catalysts. They loaded onto BNC, Pd(II) or Cu(II) salts in a sodium borohydride solution in water at 140 and 70 °C, respectively. Differences were observed in the metal catalyst's distribution, showing that Cu formed a spherical structure on the surface, while Pd nanoparticles were incorporated inside the BNC network. Furthermore, quadrupole inductively coupled plasma mass spectrometry (ICP-QMS) analysis showed that the amount of Cu on Cu/BNC was 10-fold lower than Pd on Pd/BNC, indicating more efficient incorporation for the Pd catalyst than the Cu catalyst. For this reason, the Pd/BNC catalyst was chosen for the catalytic tests. The results of the Suzuki–Miyaura reaction performed with the Pd/BNC catalyst are reported in Table 1.

As expected, the coupling reaction gave higher yields using bromobenzene **9a** with different arylboronic acids **10a–10c**, using water as an ecofriendly solvent, and highlighting the greenness of the whole process. Subsequently, the same recovered catalyst was used to catalyze the reduction of the nitro- to amino group of **11c** and **11d** with H₂, with 99% yield for both compounds (Scheme 4).

Scheme 4. Reduction of nitro-group catalyzed by Pd/BNC.

Finally, Cu/BNC catalyst was also tested for the Chan–Lam coupling reaction between benzylamine **12** and phenylboronic acid **10a** (Scheme 5). The authors supposed that the moderate observed yield was due to the low Cu incorporation on BNC. Anyway, the easy recovery and reusability, together with the negligible leaching of the metals confirmed these materials as good heterogeneous catalysts.

Scheme 5. Chan–Lam coupling reaction catalyzed by Cu/BNC.

Table 1. Pd/BNC catalyzed Suzuki–Miyaura reaction of aryl halogenides with arylboronic acid in water.

Entry	Aryl Halide	Aryl Boronic Acid	Product	Yield (%)	TON ^a	TOF ^b
1	9a	10a	11a	14	56	4.5
2	9b			78	312	26
3	9c			87	352	29
4	9c	10b	11b	77	308	26
5	9d	10a	11c	86	344	28.6
6				23 ^c	92	7.6
7		10c	11d	91	372	31

^a TON: Turnover number; ^b TOF: Turnover frequency; ^c: In the presence of Hg excess (Pd: Hg = 1:300).

2.2. Surface Chemical Functionalization of Bacterial Nanocellulose and Catalytic Applications

The introduction of sulfuric acid as functional group on the BNC surface can modify the surface polarity leading to a heterogeneous acid catalyst, with a high crystallinity and surface area. In 2018, Nikoofar and co-workers exploited this chemical modification to catalyze a multicomponent reaction in order to obtain pyrimidine fused heterocycles [39]. Multicomponent reactions (MCR) are very interesting and green tools to obtain useful scaffolds for medicinal chemistry [40]. Many green protocols have been developed in the last years [41,42], and the use of an heterogeneous catalyst can accelerate the reaction times and increases the reaction yields [43]. In this work, biodegradable and stable heterogeneous catalysts were tested in a four MCR (4-MCR). BNC sulfuric acid (s-BNC) together with nanofibrillated cellulose sulfuric acid (s-NFC) were obtained by the authors in mild condition by adding chlorosulfonic acid in n-hexane at 0 °C for 20 min. The mixture was stirred at room temperature to remove the HCl. Then, the catalysts were washed and dried to give s-BNC and s-NFC ready for the MCR reaction to give dihydropyrimido [4,5-b]quinolinetriones (Scheme 6).

Scheme 6. Multicomponent reaction catalyzed by s-BNC and s-NFC.

The reaction conditions were tested using s-NFC, which showed good results both in water and ethanol. The optimized reaction conditions were applied for both the catalysts, and the results are reported in Table 2.

Table 2. Multicomponent reactions (MCR) for the synthesis of dihydropyrimido[4,5-*b*]quinoline-triones **18a–18j** catalyzed by s-NFC or s-BNC in refluxing ethanol.

Entry	Aldehyde	Amine	Product	s-NFC		s-BNC	
				Time (Min)	Yield (%)	Time (Min)	Yield (%)
1	14a	15a	18a	45	92,90,90 ^a	40	94
2	14b	15b	18b	90	90	70	91
3	14c	15b	18c	60	85	50	83
4	14d	15c	18d	105	95	90	94
5	14e	15d	18e	90	93	80	90
6	14f	15b	18f	165	93	150	91
7	14f	15e	18g	105	95	95	90
8	14a	15f	18h	75	90	60	88
9	14g	15g	18i	75	90	65	88
10 ^b	14h	15b	18j	90	55	80	54

^a: Results for recovery and reusability of catalyst; ^b: **14h:15:16:17b** at molar ratio of 1:2:2:2 with the double amount of each catalyst.

Both the catalysts allowed the formation of the products with a range yield of 83–95% in short reaction times. In particular, s-BNC showed a short reaction time in all cases, despite its porosity reduction, if compared with the s-NFC porosity. Finally, the heterogeneous catalysts were successfully recovered and reused for the synthesis of the compound **18a** for three times.

Very recently, Said et al. developed an heterogeneous fluoride complex between BNC and tetrabutylammonium fluoride (TBAF) that allowed to be react as highly stable and selective fluoride source for fluorination reactions [44]. Although the use of a complex could be considered as out of scope for this review, this work is very interesting since the BNC was used both in batch and in flow condition with good to excellent results, demonstrating a high stability and versatility that could justify this concise regression. In brief, they tested different polysaccharides, such as BNC, vegetable cellulose, pectine, and starch, as support

for (TBAF), in order to find a stable and non-hygroscopic heterogeneous complex for the S_N2 type fluorination reactions performed both in batch and flow conditions (Scheme 7).

Scheme 7. Hydrogen bonded fluoride complexes for S_N2 fluorination reaction.

3. Cellulose Nanocrystals

Cellulose Nanocrystals (CNCs) are a particular type of nanocellulose that can be easily obtained from strong acid hydrolysis of cellulose derived from biomass or bacteria [45,46]. This non-toxic material is renewable, biodegradable and generally is provided at the ton scale through an industrial process carried out on wood pulp [47]. CNCs have numerous mechanical and physical-chemical properties such as: high crystalline order, well-defined size and morphology (generally ca. 5 nm in width and 150–250 nm in length) [48], high specific surface area, controllable surface chemistry and superior mechanical strength. These materials can be applied in different fields, including iridescent film production [49], birefringent film production [50], reinforcing fillers in plastics and polymers [51], chiral templating in carbon and silica materials [52], hydrogels [53], aerogels [54], flocculants [55], and supercapacitors [56]. They are attractive supports for various catalytically active nanoparticles (NPs), such as Pd, Au, Ag, Fe, Cu, and Ru [57], thanks to stable colloidal suspensions that form CNCs in water and for their high specific surface area which make the material highly functionalizable. Several reactions catalyzed by cellulose nanocrystals have been developed over the past five years. Below, in the following subsections, the catalytic activity of cellulose nanocrystals suitably functionalized with inorganic and organic agents will be illustrated in detail.

3.1. Inorganic Functionalization of Cellulose Nanocrystals and Catalytic Applications

Moodley and co-workers have synthesized the triazolidine-3-one derivatives with the nanocellulose (CNC)/hydroxyapatite (HAp) used as catalyst in reaction between aromatic aldehydes **20a–20l** and semicarbazide **19** with excellent yields [58]. The obtained results are reported in Table 3.

Notably, the aldehydes with both electron-donating and electron-withdrawing (*ortho*, *meta*, and *para*) substituents performed efficiently under the reaction conditions in forming the corresponding target products **21a–21l**.

Table 3. Triazolidine-3-one synthesis catalyzed by CNC/HAp.

Entry ^a	R	Product	Yield (%) ^b
1	2-OMe	21a	96
2	4-OMe	21b	96
3	4-Et	21c	95
4	2-F	21d	90
5	2-Cl	21e	94
6	4-Cl	21f	91
7	4-Br	21g	90
8	2-NO ₂	21h	92
9	3-OH	21i	93
10	2,3-(OMe) ₂	21j	94
11	2,5-(OMe) ₂	21k	94
12	3,4-(OMe) ₂	21l	91

^a: Reaction conditions: semicarbazide **19** (1 mmol), aldehyde **20a–20l** (1 mmol), catalyst (40 mg), ethanol (10 mL), room temperature. ^b: Isolated Yield.

It is possible to propose a mechanism for the cyclocondensation reaction of aldehydes and semicarbazide catalyzed by CNC/HAp (Figure 3), in which the first step starts with nucleophilic attack of NH₂ group of the semicarbazide **19** on the aldehyde carbonyl group **20a–20l** that, presumably forming a short-lived zwitterionic intermediate **22a–22l**, becomes protonated by the acidic CNC/HAp-protic solvent combination. The cyclization is completed upon elimination of water, presumably assisted by the basic form of catalyst, passing through intermediate **24a–24l**, and finally, the catalyst is released back into the catalytic cycle. Lastly, when the system is reused for further applications no significant catalyst degradation was observed for at least five runs.

Figure 3. Proposed Mechanism for the cyclocondensation between semicarbazide **19** and aldehydes **20a–20l** catalyzed by CNC/HAp.

In 2019, a composite formed by acetylated nanocellulose and nanomagnetite was prepared and tested for the esterification reaction of oleic acid **25** to obtain the corresponding methyl ester **26** for biodiesel application, as shown in Scheme 8 [59].

Scheme 8. Esterification reaction of oleic acid using cellulose-nanomagnetite Fe_3O_4 nanocomposites.

The optimal reaction conditions produced the final product in very good yields (89%) using a quantity of catalyst of 1.5 wt% and a temperature at 60 °C.

In recent work, Mirosanloo and co-workers developed an particular heterogenous nanocatalyst, composed of cellulose nanocrystals, palladium nanoparticles, and 2-aminopyridine (CNC-AMPD-Pd) and they proved its efficacy in the von Pechmann condensation of differently substituted phenols for the synthesis of coumarin derivatives [60]. The catalyst was synthesized starting from cellulose nanocrystals by a multi-step reaction reported in the Scheme 9.

Scheme 9. Synthetic pathways for the production of CNC-AMPD-Pd catalyst.

CNC-AMPD-Pd(4 mol%) was tested in reactions between substituted phenols and ethyl acetoacetate under solvent free conditions to obtain products in high to excellent yield as reported in Table 4.

The reaction yields are from good to excellent for all the substrates used, but the best yields were obtained with phenols carrying electro-donating substituents.

In another work nanocrystalline cellulose sulfuric acid (s-CNC) was synthesized by treating nanocellulose with chlorosulfonic acid in organic solvent [61]. The obtained catalyst was tested on the synthesis of polyhydroxy pyrimidine-fused heterocyclic compounds (PPFHs), starting from different carbohydrates **32–34**, different amines **35–37**, and barbituric acid **38** by a multicomponent reaction (Scheme 10).

Scheme 10. Synthesis of polyhydroxy pyrimidine-fused heterocycles(PPFHs) catalyzed by s-CNC.

Table 4. Pechman condensation of substituted phenols **29a–29m** with ethylacetoacetate **30** using CNC-AMPD-Pd(4 mol%).

	29a–29m	30		31a–31m
Entry	Phenols 29a–29m	Reaction Time (h)	Products 31a–31m	Yield (%) ^a
1		2		94
2		3		96
3		2		97
4		1.5		95
5		0.5		92
6		0.5		95
7		2		90
8		3		89
9		2		87
10		7		45
11		3		86
12		6		84
13		6		85

^a: Yields are referred to isolated product after chromatography.

The reaction was tested using different amount of the catalyst, different solvents, and different temperature. The products were obtained in short times (60–240 min) and with good yields (44–90%). The hypothesized mechanism consists in the activation of the carbonyl group of the carbohydrate by the nanocatalyst that is successively attacked by the enolic form of the barbituric acid through a Knoevenagel condensation, to produce the first intermediate. The latter is attacked by another molecule of barbituric acid by a conjugate addition followed by a dehydration to produce the second intermediate. The elimination of water leads this intermediate to a cyclization to give the final substrate that after the reaction with the amine produces the dehydrated final product.

3.2. Catalytic Transformation of Inorganic Compounds for Environmental Purposes

An et al., in 2017 [62], developed a ternary composite consisting of cellulose nanocrystal (CNC)/hexadecyltrimethylammonium bromide (CTAB)/silver nanoparticle (AgNP) used as a catalyst for reduction of 4-nitrophenol **2**. The latter is a typical polluting compound generally present in industrial and agricultural wastewater and even just a short-term inhalation can cause serious health problems such as chest pains, migraines, vomiting, stomach pain, cyanosis, and drowsiness. AgNPs immobilized on CTAB-adsorbed CNC have higher catalytic efficiency towards the reduction of 4-nitrophenol **2** to 4-aminophenol **6**, compared to the control AgNPs and CNC/Ag samples. The improved catalytic performance of AgNPs immobilized on CTAB-adsorbed CNC was attributed to the better dispersity and narrow distribution of silver nanoparticles in the catalytic system thanks to both surfactant ability of the alkyl chain of CTAB that favors hydrophobic interactions with nanoparticles and quaternary ammonium group that increases hydrophilic interaction with CNC. The resulting ternary nanocomposite was applied for highly efficient catalytic reduction of 4-nitrophenol (4-NP) **2** to 4-aminophenol (4-AP) **6**. The composite was prepared using cellulose nanocrystals obtained from cellulose pulp subjected to acid hydrolysis using 64 wt% sulfuric acid. The resulting CNC was dispersed in water by the application of ultrasound and, subsequently, the surfactant CTAB at pH = 4.5 was introduced. The loading of the nanoparticles on the composite was favored by the introduction of silver nitrate which was subsequently reduced to silver NPs using NaBH₄. It should be stressed that novel small-sized molecules behaving as amphiphiles are currently being studied thanks to their ability to form ionic liquids [63]. Such molecules, belonging to alkylphosphate, alkylamine [64], or carboxylic acids [65], are stimulating great interest due, for instance, to the peculiar self-assembly that they can trigger [66]. For this reason we believe that interesting uses/ applications can be foreseen if such amphiphiles are used with nanoparticles, as for the example given for CTAB/AgNPs. It should be also said that silver nanoparticles can be easily prepared in conjunction with titania in an interesting nanocomposite with metal-semiconductor junction, which can have, obviously, particular electronic properties [67].

In any case, in the work reported by An et al. [62] the reduction of 4-NP **2** with NaBH₄ was applied as model reaction to determine the catalytic activity of CNC/CTAB/Ag nanohybrid composite as reported in Scheme 11.

Scheme 11. Catalytic reduction of 4-nitrophenol **2** by NaBH₄ in the presence of CNC/CTAB/Ag nanohybrid composite.

Upon the addition of NaBH_4 in the 4-NP **2** solution, the 4-nitrophenolate ion **48** is generated. Then, after the addition of CNC/CTAB/Ag nanohybrid composite, the anion specie is reduced to amino compound **6**. The results revealed that CNC/CTAB/Ag nanomaterial possessed the high catalytic activity for the 4-nitrophenol reduction, compared with those of unsupported Ag NPs and CNC/Ag nanocomposite, thanks to the uniformly dispersed Ag NPs with narrow size distribution. The catalytic activity (545 h^{-1}) and pseudo-first order rate constant ($k = 1.6 \times 10^{-3} \text{ s}^{-1}$), were determined for the CNC/CTAB/Ag nanohybrid composite and these results indicated that the system has great potential in catalytic treatment of industrial and agricultural wastewater.

Another catalyst used for reduction of 4-nitrophenol **2** was synthesized by Zhang et al. in 2018 [68]. A simple and performant one-pot synthesis of well-dispersed hollow CuFe_2O_4 nanoparticles (H- CuFe_2O_4 NPs) in the presence of cellulose nanocrystals (CNC) as the support was described in this study. Based on the one-pot solvothermal condition control, magnetic H- CuFe_2O_4 nanoparticles were in situ grown on the CNC surface uniformly. The catalytic activity of H- CuFe_2O_4 /CNC was verified in the reduction of 4-NP **2** (Scheme 12).

Scheme 12. Catalytic reduction of 4-nitrophenol by NaBH_4 in the presence of H- CuFe_2O_4 /CNC composite.

The catalytic system exhibited an excellent performance compared to classical CuFe_2O_4 NPs, which was attributed to the introduction of CNC and the special hollow mesostructure of H- CuFe_2O_4 NPs. In addition, the H- CuFe_2O_4 /CNC was recovered and reused for at least 10 times in the corresponding reactions without significant deactivation in the catalytic activity, confirming relatively high stability.

Moreover, Dhar and co-workers [64] used this catalyst for the reduction of 4-nitrophenol **2** into 4-aminophenol **6** as indicated in Scheme 13, observing quantitative conversion as also proved by UV-visible absorbance analysis.

Scheme 13. Conversion of 4-AP **6** to 4-NP **2** catalyzed by CNC-supported zerovalent iron nanoparticles (ZVIs).

Another magnetic composite based on MnFe_2O_4 /cellulose nanocrystal was synthesized in 2018 for the catalytic decomposition of methylene blue **1** (MB) [69]. The nanocomposite was prepared starting from the cellulose hydrolysis for nanocellulose preparation. The obtained CNC was mixed with MnCO_3 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ under alkaline conditions. The resulting material, namely MnFe_2O_4 /CNC, displayed high specific surface area and small particle dimension. It showed a higher catalytic activity than MnFe_2O_4 for the decomposition of MB **1** in H_2O_2 solution. Furthermore, MnFe_2O_4 /CNC demonstrated a high

recovery on application of a magnet in the reaction system, which suggests great potential for wastewater purification.

Cellulose nanocrystals obtained from renewable bamboo pulp were used by Dhar and co-workers as a support for zerovalent iron nanoparticles (CNC-supported ZVIs), for multiple applications [70]. They proved that CNC-supported ZVI catalyst can be used for wastewater remediation for the decomposition of MB 1. The decomposition was proven to be almost quantitative by UV-visible absorbance analysis. The hypothesized decomposition products, suggested by GC-MS studies, was reported in the following scheme (Scheme 14).

Scheme 14. Hypothesized decomposition pathways of methylene blue 1.

3.3. Synthetic Applications of CNCs Grafted with Inorganic Catalysts

Goswami and Das have synthesized cellulose impregnated copper nanoparticles (CNC/CuNPs) used as heterogeneous catalyst for aza-Michael reactions, involving open chained as well as cyclic secondary amines and vinylic compounds directly bonded at electron-withdrawing group, to synthesize *N,N*-disubstituted 3-aminopropanoate esters or *N,N*-disubstituted 3-aminopropanenitriles (Table 5) [71].

Table 5. aza-Michael reaction between different amines and electron deficient vinylic compounds.

Entry ^a	Amine 51a–51f	Vinylic Compound 52–53	Product 54a–54f, 55a–55f	Time (h)	Yield (%)
1	Et ₂ NH			0.75	93
2	Et ₂ NH			1	90
3				1.5	92
4				1.5	88
5	iPr ₂ NH			3.5	82
6	Bn ₂ NH			2	93
7	Bn ₂ NH			1.5	88
8				0.75	95
9				0.75	95
10			No product	24	-
11			No product	24	-

^a 1.1 mmol of amine 51a–51f react with 1.0 mmol of vinylic compound 52–53. Mass of Methyl acrylate taken is 86.09 mg and mass of Acrylonitrile taken is 53.06 mg. iPr is isopropyl group and Bn is benzyl group.

The heterogeneous catalyst demonstrated excellent yield (82–95%) probably due to high reduction potential of copper (indicating strong oxidizing character) which ensures greater compatibility with electron rich groups like amines. However, it was found to be totally inert when used in the case of aromatic amines (Table 5, entries 10 and 11). Finally, the catalyst can be easily recovered from the reaction mixture and reused several times without any significant loss of activity.

In 2017, Chetia et al. used CNC/CuNPs to synthesize a series of 1,4-disubstituted 1,2,3-triazoles **67–80** by azide-alkyne cycloaddition carried out in glycerol, an environmentally benign solvent, with reaction yields ranging from 68% to 99% [72]. In particular, 1,2,3-triazoles are five-member N-heterocyclic compounds bearing three nitrogen atoms in the ring that can be easily synthesized in regioselective and eco-friendly way [73–76], giving products with notable biological activities [77–79]. Generally, 1,3-dipolar cycloaddition reaction, are considered a useful approach for the synthesis of bioactive heterocyclic compounds [80,81], sometimes enhancing the biological value already possessed by the precursors involved [82]. However, the results obtained from Chetia and co-workers are summarized in Table 6.

Table 6. CuNP-CNC-catalyzed 1,3-dipolar cycloaddition reaction between azides and alkyne.

Entry ^a	R ₁	R ₂	R ₃	Product	Time, t (h)	Yield (%) ^b
1	Bn	Ph	H	67	1.5	99
2	Ph	Ph	H	68	1.5	98
3	4-Br-Ph	Ph	H	69	4	70
4	4-Cl-Ph	Ph	H	70	4	69
5	4-MeO-Ph	Ph	H	71	2	98
6	4-CN-Ph	Ph	H	72	4	68
7	C ₈ H ₁₇	Ph	H	73	2	97
8	4-Br-Ph	C ₄ H ₉	H	74	4.5	82
9	Bn	C ₄ H ₉	H	75	3.5	83
10	Ph	C ₄ H ₉	H	76	1.5	99
11	Bn	CH ₂ OH	H	77	2.5	71
12	4-Br-Ph	CH ₂ OH	H	78	3.5	72
13	Ph	CH ₂ OH	H	79	3	93
14	Ph	COOMe	COOMe	80	3.5	89

^a: Reaction is performed with 1 mmole of azide **56–62**, 1.1 mmole of alkyne **63–66** and 1.05 mol% of heterogeneous catalyst in 2 mL of glycerol at room temperature. ^b: Isolated Yield.

The application of this kind of reaction, using CuNPs/CNC as heterogeneous catalyst, was investigated with different azides and alkynes and the best conditions were found at room temperature. Aromatic and aliphatic terminal alkynes readily reacted with the diverse azides to give the corresponding 1,4-disubstituted 1,2,3-triazoles **67–80** in good to excellent yields (68–99%). High reaction yields are observed when phenylacetylene reacts with aromatic or alkylic azide (entries 2, 10, 13, 14). The recyclability of CuNPs/NC was investigated in the cycloaddition of phenylacetylene **63–66** and benzylazide **56** and after each cycle the catalyst was recovered by simple filtration and reused after washing with organic solvent. About 90% of the original activity was obtained even after the fifth run. In a work carried out by Dutta and co-workers, Cu nanoparticles were immobilized on nanocellulose, producing CuNPs/CNC material that was tested as heterogeneous catalyst for the oxidation of sulfides in mild reaction conditions, good yields, and discrete reaction time. Sulfides are versatile compounds also present in nature, with important pharmacological activity [83], which can be synthesized through easy approaches [84].

The results are collected in Table 7 [85].

Table 7. Oxidation of sulfides by CuNPS/CNC in ethanol.

$\text{R}_1-\text{S}-\text{R}_2 \xrightarrow[\text{EtOH}]{\text{CuNPs/CNC, H}_2\text{O}_2} \text{R}_1-\text{S}(=\text{O})-\text{R}_2$				
81a–81f		82a–82f		
Entry	Substrates 81a–81f	Products 82a–82f	Time (h)	Yield (%) ^a
1			2	99
2			5	95
3			12	73
4			12	65
5			2	96
6			2.5	95

^a: Isolated yield.

The developed catalyst was also tested on the oxidation of different alcohols using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as nitroxyl radical and the results are reported in Table 8.

Table 8. Oxidation on different alcohols by CuNPs/NC and TEMPO.

83a–83h	84a–84h		
Entry	Substrates 83a–83h	Products 84a–84h	Yield (%) ^a
1			99
2			82
3			95
4			95
5			98
6			80
7			45
8			45

^a: Isolated yield.

The reaction outcome was excellent predominantly with *para*-substituted aromatic alcohols. Lower yield was observed for saturated and unsaturated aliphatic alcohols probably due to the steric hindrance of the long alkyl chains. These latter, generally, are introduced on organic molecules to enhance the biological activity [86]. Nanocomposites with diameters less than 100 nm, used as heterogeneous catalysts, are difficult to separate from the reaction mixture. Therefore, the adsorption of magnetic nanoparticles on their surface furnish a facile-apply magnetic material that can be recovered by simple attraction

from an external magnet [87]. In this context, Mirjalili and Imani synthesized a magnetic bio-based nanocatalyst, signed as $\text{Fe}_3\text{O}_4@\text{CNC}/\text{BF}_{0.2}$ (where BF is referred to $\text{BF}_3 \cdot \text{OEt}_2$) for the synthesis of aryl-2,3-dihydro-1H-perimidines **87a–87l** by cyclocondensation of 1,8-diaminonaphthalene **86** with aromatic aldehydes **85a–85l** (Table 9) [88].

Table 9. Synthesis of aryl-2,3-dihydro-1H-perimidine derivatives with $\text{Fe}_3\text{O}_4@\text{CNCs}/\text{BF}_{0.2}$ used as catalyst.

Entry ^a	R	Time (min)	Product 87a–87l	Yield (%) ^b
1	H	5	a	98
2	4-OMe	15	b	91
3	4-NMe ₂	15	c	86
4	2,4-(OMe) ₂	15	d	75
5	3,4-(OMe) ₂	15	e	92
6	4-Cl	10	f	96
7	4-COOH	10	g	99
8	2-NO ₂	12	h	94
9	3-NO ₂	10	i	96
10	4-NO ₂	10	j	99
11	2,3-(OMe) ₂	20	k	85
12	2,3-(Cl) ₂	15	l	88

^a: aldehyde **85a–85l** (1.0 mmol), 1,8-diaminonaphthalene **86** (1.0 mmol) and $\text{Fe}_3\text{O}_4@\text{CNCs}/\text{BF}_{0.2}$ (0.03 g) are stirred at room temperature for the opportune time. ^b: Isolated Yield.

In Table 9, it is possible to observe good and high yields of products under very mild and green conditions and short reaction time. Moreover, the presence of electron-withdrawing groups on the aromatic ring of the aldehyde favors the formation of the product with higher yields than the presence of electron-donating groups. Other advantages of $\text{Fe}_3\text{O}_4@\text{CNCs}/\text{BF}_{0.2}$ as a catalyst are biodegradation, reusability, environmental friendliness, and easy separation with an external magnet. The recyclability of the catalyst was also investigated on the model reaction (Table 9, entry 1), reusing it at least four times with little loss of catalytic activity. The proposed mechanism is shown in Figure 4.

The proposed mechanism consists of a series of stages. At first, $\text{Fe}_3\text{O}_4@\text{CNCs}/\text{BF}_{0.2}$ as Lewis acid attacks the carbonyl group of the aldehyde **85a–85l**, generating the imine intermediate **92a–92l**. The latter cyclizes by intramolecular nucleophilic attack of amino group present on the naphthalene backbone, affording the products **87a–87l**. In summary, this method offers different advantages including easy work-up, high yields in short time and the heterogeneous catalyst is eco-friendly because it can be reused for numerous cycles.

Liu et al. proposed new catalysts based on cellulose nanocrystals supported dirhodium (II) to be investigated on the cyclopropanation of styrene with EDA [89]. The catalytic systems were abbreviated in CNC-Rh₂-0.5d, CNC-Rh₂-2.5d, and CNC-Rh₂-4.5d. Among these species CNC-Rh₂-4.5d was selected for testing it on the model reaction because it showed the highest concentration of catalytic sites. The reaction Scheme and the yields of the products are reported in Table 10.

Figure 4. Proposed Mechanism for the synthesis of aryl-2,3-dihydro-1H-perimidines **87a–87l** catalyzed by $\text{Fe}_3\text{O}_4\text{@CNCs/BF}_{0.2}$.

Table 10. Reaction of styrene with EDA catalyzed by CNC-supported rhodium catalyst.

Entry ^a	Reaction Time	<i>Cis</i> -97 Yield (%)	<i>Trans</i> -97 Yield (%)	Total Yield (%)
1	15	20	22	42
2	30	21	29	50
3	45	28	34	62
4	60	29	35	64
5	120	33	39	72
6	180	34	40	74

^a: The reaction was tested using the CNC-Rh₂-4.5d catalyst.

Finally, the recyclability of the catalyst CNC-Rh₂-4.5d was also evaluated, demonstrating that the yields remained almost unchanged after three cycles.

4. Cellulose Nanofibers

With the term cellulose nanofibers (CNFs), also named cellulose nanofibrils, nanofibrillated cellulose, and nanofibrous cellulose, is intended a wide family of nanocelluloses characterized by a nanometric length comprised between 50 and 3000 nm and a width from 5 to 50 nm. Introduced in early 1980s [90,91], CNFs are obtained from the mechanochemical treatment of cellulosic biomasses, and presents a lower degree of crystallinity with respect to cellulose nanocrystals or bacterial nanocellulose. In addition, they also show interesting mechanical and physicochemical properties: large specific surface area, high strength, and an easy chemically tunable surface.

At the beginning, CNFs were obtained from the simple delamination of delignified and bleached pulps; however, this treatment has been shown to be very expensive in terms of energy consumption, and various other mechanical procedures have been proposed to improve this aspect and making the industrial production of CNFs much more affordable [92–94]. Numerous other procedures have been also developed in order to improve further the production of CNFs and can be categorized into two main families: swelling induced by charged groups, enzymes [95,96], or mild acid treatments. In the first case, the main procedures employed to introduce charged groups in the polymeric backbone include chemical oxidation performed via TEMPO (2,2,6,6-tetramethyl piperidinyloxy) [97,98] and carboxymethylation [99].

In this section, we will focus on the catalytic applications of inorganic and organic-functionalized CNFs. For a broader review of the production and applications of CNFs, the reader can refer to [97,100–102].

4.1. Inorganic-Functionalized CNFs Employed in Catalysis

The inorganic functionalization of CNFs for catalytic applications is mainly devoted to the use of CNFs as supporting materials for the growth of nanoparticles (NPs). The NPs mainly used as heterogeneous catalysts are made up including noble and transition metals such as Bi, Al, Mo, Ag, Fe, Ti, Ru, Cu, Co, Pt, Pd, Ni, and Au, often in their oxidized state or in presence of another element (i.e., Ni/Fe, CoS, CuS, etc.). The main fields of application reported in literature comprise catalytic degradation of environmental pollutants, electrocatalytic conversion of small molecules, photocatalysis and organic synthesis.

4.1.1. Catalytic Transformation of Organic Compounds for Environmental Purposes

Chemical transformation of organic and inorganic pollutants can be a useful strategy for pollutants removal in aqueous systems. In this sense, Ag-based CNF composite proved to be an efficient medium for the conversion of diverse chemicals having high environmental impact. The principal applications of Ag NP-decorated CNFs consist of degradation of dyes in aqueous systems or reduction of nitrophenolic derivatives. One of the first evidences about aqueous dyes degradation was reported in literature by Jang and co-workers with the evaluation of the role of a deacetylated-CNF template included in AgNP growth and the efficacy of the composite in methylene blue (MB) reduction [103]. The composite was tested evaluating the degradation of MB measuring the intensity of the main absorption peak of the dye at 668 nm, revealing that the full dye degradation took place in 1–10 min.

Recently, Zhang and collaborators developed a new CNF-hydrogel poly(ethylene imine)-based material functionalized with Ag NPs [104]. The material was tested on catalytic continuous discoloration of aqueous cationic and anionic dyes in batch and in flow test obtaining an efficiency greater than 98% maintained for up to 10 cycles of employ. The possibility of using this membrane material under high water flux ($5 \times 10^4 \text{ L} \cdot \text{m}^{-2} \text{ h}^{-1}$) allowed the treatment of considerable volumes of water.

As for nitrophenols degradation, one of the first evidences was reported by Heidari [105]. In this reported case, the composite was prepared adsorbing Ag NPs on hydrogels of CNFs, which was a non-inert template since it acted also as a stabilizer and reducing agent toward the pollutants employed. Its catalytic potency was evaluated, in particular, toward the degradation of **2** to **6** (Table 11), obtaining values of rate constants up to $46.6 \times 10^{-3} \text{ s}^{-1}$ and catalytic activities up to $2.33 \text{ s}^{-1} \text{ g}^{-1}$. In another work, Gopiraman and collaborators realized Ag NP-decorated CNFs that were tested toward the reduction of both **2** and **5** in water. The reported rate constants for the two pollutants were, respectively, $9.05 \times 10^{-2} \text{ s}^{-1}$ and $11.34 \times 10^{-2} \text{ s}^{-1}$, showing very important results [106]. Successively, in 2019, they proposed a new Ag@Au bimetallic CNF composite from leaves of *Moringa oleifera* [107]. The catalytic performance of Ag@Au@CNFs was evaluated on a solution of nitrophenol measuring the UV-vis absorbance of the nitrophenol in the sample at different

intervals. Table 11 summarizes the evidence reported in literature about nitrophenols (NP) reduction employing Ag NP-functionalized CNFs.

Table 11. Applications of Ag NPs@CNFs catalysts to 4-NP **2** and 2-NP **5** reduction in water.

R = 2-NO₂, 4-NO₂ R = 2-NH₂, 4-NH₂

2, 5 **6, 8**

Nitrophenol (NP)	Catalyst	Rate Constant	Reference
2	Ag/CNFs hydrogel	$46.6 \times 10^{-3} \text{ s}^{-1}$	[105]
2	Ag/CNFs	$9.05 \times 10^{-2} \text{ s}^{-1}$	[106]
5		$11.34 \times 10^{-2} \text{ s}^{-1}$	
2	Ag/Au/CNFs	$22.83 \times 10^{-2} \text{ s}^{-1}$	[107]
5		$15.59 \times 10^{-3} \text{ s}^{-1}$	

Iron too was explored as inorganic-functionalizing agent for CNF hybrid material production. Cunha Arantes and collaborators proposed an hybrid catalyst made up of CNFs and iron oxide NPs (magnetite) [108]. This catalyst was employed in MB degradation in a Fenton-like process which degraded 100% of dye in 180 min. Iron-based CNF nanocatalyst was explored also using Fe elements in combination with other metals as reported by Hou, very recently [109]. In this regard, Fe was employed in combination with Co in order to obtain a metal–organic framework (MOF) adsorbed onto the surface of CNFs. This approach enabled a membrane to be obtained useful for the catalytic degradation of tetrabromobisphenol A (TBBPA), a widely dispersed brominated flame retardant (BFR) also known for its hepatotoxicity, cytotoxicity, and immunotoxicity. In this case, Co/Fe bi-MOF/CNF composite was capable of full degradation of TBBPA in 30 min with rate constant of 0.764 min^{-1} and a degradation of the catalytic membrane of 60% after four cycles of treatment.

In 2018, Pd NPs were employed in the preparation of reusable CNFs water-activated shape memory aerogels [110]. The material was obtained starting from TEMPO CNF-derivatives and applied for the catalytic degradation of both cationic and anionic dyes (MB **1** and Congo red) at concentration of 20 ppm, giving a discoloration efficiency comprised between 91.1 and 99.0% for five cycles of work.

Ujihara and co-workers were capable of preparing in 2018 a new composite where Pt NPs were embedded by a nanostructure of dendrimers and cellulose nanofibers [111]. In this case, the dendrimer was made up of poly (amido amine) and was covalently bonded on 2,2,6,6-tetramethyl-1-piperinyloxy free radical oxidized cellulose nanofibers (TOCNFs). The prepared Pt-based composite were successfully applied to catalytic degradation of formaldehyde and **5**. In 2020, a composite material made up by borate-functionalized CNFs and Pt (or Ag and Au) was prepared for application in degrading of 4-nitrophenol **2** [112]. In this study, functionalized CNFs acted as reducing agents in order to obtain the NPs on their surface, giving nanospheres of diameters of 9 nm. Their activity in 4-nitrophenol **2** degradation was quantified calculating their TOFs numbers, giving values comprised between $1038 \pm 238 \text{ h}^{-1}$ (Pt NPs/CNFs suspension) and $352 \pm 34 \text{ h}^{-1}$ (Ag@Pt NPs/CNF-B(1%) film).

In 2020, other evidence about inorganic elements employed in this context were reported by Idrissi et al. [113]. In this context, the role of Co NPs on the surface of CNFs was investigated for the reduction of 4-nitrophenol **2** that was successfully reduced in 8 min at 25 °C. Gan and co-workers, again in 2020, focused on the role of polyoxometalate in combination with carbonized cellulose nanofibers [94]. They applied this type of

composite on oxidative desulfurization reactions, a promising procedure for the removal of sulfur-based heterocyclic derivatives. In this work, the polyoxometalate chosen was $[\beta\text{-SiMo}_3\text{W}_9\text{O}_{40}]^n$, which was loaded on the CNF's surface. The removal of dibenzothiophene, benzothiophene and 4,6-dimethyldibenzothiophene in oil was quantified, giving reduction percentages up to 99%. In a similar way, Zhang et al. reported the hydroxydesulfurization of dibenzothiophenes achieved through mesoporous $\gamma\text{-Al}_2\text{O}_3/\text{CNFs}$ acting as template for MoNi NPs as catalyst; in this case, k and TOF parameters obtained were up to $16.9 \times 10^{-4} \text{ mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and 5.3 h^{-1} , respectively [114].

4.1.2. Electrocatalytic Applications of Inorganic-Functionalized CNFs

The main application of inorganic-CNF composites in electrocatalysis involves oxygen transformations and, in particular, the so-called oxygen evolution reactions (OERs) and oxygen reduction reactions (ORRs) (Figure 5).

Figure 5. Example of a typical oxygen evolution reaction (OER) and oxygen reduction reaction (ORR).

OERs are an important class of electrochemical reactions which enable the production of hydrogen from water-splitting, particularly employed in fuel cells, solar cells, and metal–air batteries. In this regard, Tian and collaborators reported in 2019 the first evidence of a CNF-based template for the preparation of electrocatalysts to employ in OERs [115]. In particular, it was realized that a Ni/Fe/CNFs composite where the abundance of carboxyls and hydroxyls groups present on the surface of CNFs helped the fine dispersion of the inorganic moiety. This material exhibited a very high electrocatalytic performance and an excellent long-term stability.

Subsequently, Tao and collaborators successfully employed a Ni derivative to functionalize N-doped CNFs [116], where the term “N-doped” stands for CNFs with a nitrogen content via a pretreatment with dicyandiamide. In this case, Ni@Ni₂P NPs grafted onto a carbonized composite of CNFs and carbon nanotubes, taking advantage from the notable specific surface area present. The obtained catalyst enabled an overpotential of 269 mV to be achieved, with a 1.7% decay after 20 h long-term test. In the same year, Tian et al. [117] developed a CoFeS@CNFs nanocomposite which achieved an overpotential of 257 mV while delivering a current of $10 \text{ mA}\cdot\text{cm}^{-2}$ and decreasing by only 2.82% after 50 h of work.

As for ORRs, Lee et al. [118] and Meng and co-workers [119] proposed important evidence in this field of fuel cells science. In the first case, a nanocomposite based on TEMPO-oxidized N-doped porous carbon CNFs decorated with Co@Co₃O₄ NPs was reported. Even in this case, a three-dimensional network of the CNF template helped the fine dispersion of the catalyst's NPs, giving performances comparable to the already-used Pt/C catalysts. As for the other reference, a nanocomposite made up by Co NPs loaded on N-doped CNFs was prepared. The catalyst reported notable properties, like a long-term durability, becoming an important alternative to the available Pt/C systems.

4.1.3. Photocatalytic Applications of CNFs-Inorganic Composites for Environmental Remediation

The main photocatalytic applications of inorganic-functionalized CNFs concern the chemical transformation of organic and inorganic species considered dangerous pollutants even at low concentrations. In particular, they have been applied in the catalytic degradation of dyes, dangerous cationic metals, and antibiotics.

In 2018, Salama and co-workers prepared a composite material made up from CA-CNFs, multiwall carbon nanotubes (CNT), and NH_2 -functionalized TiO_2 NPs [120]. The so-obtained material was successfully employed in photodegradation experiments with MB and indigo carmine (IC), revealing degradation percentages up to 100% for both dyes. In this case, factors such as temperature, pH, and power intensity of the UV lamp were investigated to find the best conditions. Zabihi Sahebi et al. also developed a CNF-based inorganic composite useful in photocatalytic degradation of dyes and harmful inorganic species [121]. In this case, CA/chitosan/single walled CNT/ Fe_3O_4 / TiO_2 nanofibrils were obtained via electrospinning technique and applied to the removal of MB, Congo red, Cr(VI), and As(V). In particular, this material enabled the complete degradation of both organic and inorganic pollutants up to concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ to be achieved. For Cr(VI) and As(V), the composite showed a notable degradation percentage (95%), while the percentage lowered to 85% for both the aza-dyes.

Another approach for Cr(VI) removal was recently proposed by Gan and collaborators [122]. They prepared a series of cellulose-derived carbon nanofibers which were then combined with bismuth oxybromide (BiOBr). In this case, the catalyst generated active oxidative and reductive oxygen species in situ capable of simultaneously degrading Cr(VI) and rhodamine B (RhB) dye at an initial concentration of $10 \text{ mg}\cdot\text{L}^{-1}$ for both species. In particular, it was established that the presence of RhB in the aqueous system promoted the removal efficiency of Cr(VI).

RhB was also subject of study in the study proposed by Tian and co-workers [123]. In this case, a composite where CNFs were employed to anchor Ag ions onto carbon nitride (CN), an interesting metal-free photocatalyst. This approach guaranteed an efficient degradation of RhB and tetracycline (TC) under visible light was realized.

Other important evidence useful in dye remediation of waters was recently proposed by several authors employing bimetallic systems. In particular, Gupta and collaborators proposed a novel CNFs-based composite bearing NiFe_2O_4 NPs applied to the photo-Fenton degradation of Remazol Black 5 (RB5) and nitrophenols 2 and 5, obtaining interesting results [124]. Zheng et al., on the other hand, developed a bimetallic system Co-Cu-based (CoS_2 -CuS) particularly active in antibiotics degradation [125]. The drugs chosen for this study were ciprofloxacin and ofloxacin: under UV-light, at pH 5 and in 60 min, their CoS_2 -CuS@CNFs novel catalyst was capable of degrading up to 98.11% and 88.0%, respectively, of each compound. Zhang and co-workers [126] also recently introduced a novel bimetallic derivative for photocatalytic purposes. The realized material was a membrane consisting of CNFs- CoFe_2O_4 /PVDF (polyvinylidene fluoride) used in the cathode of a photocatalytic fuel cell (PFC). In this case, the material was capable of activating peroxymonosulfate (PMS) transformation in order to obtain sulfate radicals (SO_4^-), hydroxyl radicals (OH), singlet oxygen ($^1\text{O}_2$), and superoxide radical (O_2^-). The species obtained took part in the subsequent degradation of berberine, an antibiotic, shading new light on PFC/PMS systems applied to water remediation. Table 12 summarizes the photocatalytic applications of inorganic-containing CNFs described in this section.

Table 12. Resume of the photocatalytic applications of inorganic-containing CNFs.

Substrate	Catalyst	Reference	Substrate	Catalyst	Reference
MB 1	Ag@CNFs TiO ₂ - NH ₂ @CNFs/CNT Fe ₃ O ₄ /TiO ₂ @CNF/ Chitosan/CNT	[120] [121]	2 25	NiFe ₂ O ₄ @CNFs	[124]
Indigo carmine	TiO ₂ - NH ₂ @CNFs/CNT	[120]	Cr(VI)	Fe ₃ O ₄ /TiO ₂ @CNF/ Chitosan/CNT BiOBr@CNFs	[121] [122]
TC	Ag/CN@CNFs	[123]	As(V)	Fe ₃ O ₄ /TiO ₂ @CNF/ Chitosan/CNT	[121]
Congo red	Fe ₃ O ₄ /TiO ₂ @CNF/ Chitosan/CNT	[121]	Ciprofloxacin Ofloxacin	CoS ₂ -CuS@CNFs	[125]
RB5	NiFe ₂ O ₄ @CNFs	[124]	PMS	CNFs- CoFe ₂ O ₄ /PVDF	[126]
RhB	BiOBr@CNFs Ag/CN@CNFs	[122] [123]			

4.1.4. Synthetic Applications of CNFs Grafted with Inorganic Catalysts

The role of inorganic-functionalized CNFs in organic synthesis has been greatly extended in the last years, allowing notable development in the synthesis of compounds of high industrial interest. The main applications reported in literature are summarized in Figure 6.

Figure 6. Catalytic applications of inorganic functionalized CNFs.

Hydroboration of alkynes **98a–98i** using CNFs as template for inorganic catalysts was recently proposed by Zhang et al. [127]. In their work, functionalized CNFs were firstly

functionalized via hydrolytic silane condensation in order to obtain their thiolated-form and, subsequently, employed as template for the immobilization of Cu(I) cations. As result, the CNFs-based nanosponges obtained showed high porosity and low density. The material was successfully tested as heterogenous catalyst, giving alkenes **99a–99i** in excellent yields and up to 99% of regioselectivity. Furthermore, the reusability of the material was tested guaranteeing optimal catalytic performances until six reaction cycles. The reaction partners involved are reported in Table 13.

Table 13. Hydroboration of alkynes **98a–98i** using a Cu@CNFs heterogeneous catalyst.

$$\text{R}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{EtOH (2 eq.), 25 }^\circ\text{C}]{\text{[Cu] (4\%), NaOMe (20\%)}, \text{B}_2(\text{pin})_2 \text{ (1.5 eq.), DMF (2 mL)}} \text{R}-\text{CH}=\text{CH}-\text{B}(\text{pin}) + \text{R}-\text{CH}=\text{CH}-\text{B}(\text{pin})$$

	98a–98i	99a–99i		
Entry	Reactant	Product	Conv. (%)	E/Z
1			92	99:1
2			97	99:1
3			92	97:3
4			97	99:1
5			97	98:2
6			99	>99:1
7			99	99:1
8			92	99:1
9			86	99:1

As for alcohol oxidation, an interesting example was presented by Gopiraman and co-workers in 2015 [128]. In this case, they were able to employ acetate-derivatives of CNFs in order to obtain anionic cellulose nanofibers (CNFs) acting as template for noble metal particles adsorption. The metals at the center of this work were Ru and Ag. The catalytic evaluation of the Ru-containing composite was tested on the aerobic conversion of benzyl alcohol to benzaldehyde, furnishing yields up to 89% and with 100% of selectivity. For the Ag-based composite, the model reaction was the *aza*-Michael coupling between **100** and **101** giving yields of 99% and 100% selectivity. The catalytic cycle proposed for this reaction is illustrated in Scheme 15.

CNF derivatives as heterogeneous catalyst were also tested in Suzuki couplings, as reported by Jebali and collaborators [129]. In this regard, CNFs were employed in their cationic form in order to maximize the adsorption of Pd NPs via in situ reduction of PdCl₂. This simple approach gave a Pd-containing nanocomposite which was tested as catalyst on the coupling between aryl halides **102a–102g** and arylboronic acid **10a**. The results, listed in Table 14, report an almost quantitative reaction yield; in addition, several reusability tests were successfully performed obtaining the above reported performances up to three catalytic cycles.

Scheme 15. Catalytic cycle proposed by Gopiraman and co-workers for the CNFs@Ag NPs-catalyzed aza-Michael coupling of 1-phenylpiperazine **100** and acrylonitrile **101**.

Table 14. Suzuki coupling using Pd@CNF catalyst.

$\text{R}-\text{C}_6\text{H}_4-\text{X} + \text{C}_6\text{H}_5-\text{B}(\text{OH})_2 \xrightarrow[\text{DMF}]{\text{Pd@CNF, K}_2\text{CO}_3} \text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$					
Entry	ArX	Conv. (%)	Entry	ArX	Conv. (%)
1		98	2		98
3		93	4		99
5		87	6		68
7		96			

A notable application of aerogel CNFs as catalytic templates was reported by Hees et al. in 2017 [130]. In this case, nanocellulose aerogels were obtained freeze-drying CNFs and subsequently impregnated with methylaluminoxane. This organic layer worked as support for the immobilization of bisiminopyridine iron(II) complexes, which served as catalyst for the low-pressure polymerization of ethylene.

Last, but not least, two important catalytic applications of inorganic-functionalized CNFs were proposed by Koga [131] and Ghamari Kargar and respective collaborators [132]. In the first case, the catalyst was prepared from CNFs decorated with Cu(I). The latter was

employed with respect to the Huisgen [3+2] cycloaddition reaction involving benzylazide **104** and phenylacetylene **105** obtaining 1,2,3-triazoles 1,4-disubstituted in high yields (Figure 7).

Figure 7. $Fe_3O_4@CNF$ -ImSalophCu-catalyzed mechanism for 1,4-disubstituted 1,2,3-triazoles synthesis.

In the second case, the research group of Ghamari Kargar proposed a new approach for the synthesis of 1,2,3-triazole derivatives employing the $Fe_3O_4@CNF$ -ImSalophCu nanocatalyst illustrated in Figure 8. Particularly, it was realized the one-pot three component reaction between phenacyl bromides, sodium azide and alkynes, obtaining 1,4-disubstituted 1,2,3-triazoles in yields up to 98%.

Figure 8. $Fe_3O_4@CNF$ -ImSalophCu nanocomposite.

4.2. Organic-Functionalized CNF Employed in Catalysis

The use of CNFs derivatives enriched with organic moieties for catalytic applications have recently seen interesting developments in diverse fields of organic synthesis. In 2018, two important applications were proposed. In the first example, TEMPO-oxidized CNFs (TOCNs) were successfully applied as organocatalysts in hydrolysis of acetals **106** to aldehydes **107** [133] (Scheme 16) with very good performances and quantitative yields.

diketones in water at room temperature. This approach enabled yields up to 96% and to be achieved interesting reusability properties.

5. Conclusions

NCs represent an important contributor to chemical synthesis in terms of eco-sustainability and efficiency. In this regard, this review fills the lack of totally focused overview on inorganic and organic-decorated NCs as heterogeneous catalysts. In particular, BNC and CNFs are shown to possess promising properties in terms of both inorganic and organic-mediated catalysis, while CNCs reveal themselves to be a powerful tool as template for the grow of metallic NPs-catalysts, and in particular for the transformation of chemicals for environmental purposes. Nonetheless, it is conceivable that there is a synergistic contribution between the functional portion of the catalyst (NPs, organic framework, etc.) and its polysaccharidic backbone, making the entire nanomaterial a “non-innocent” template. These aspects, united with the numerous examples in terms of easy disposability, reusability, cheapness, and high chemical tunability of the catalysts reported above, increasingly enhance the central role assumed by NCs in chemistry.

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