Effects of Metal Ions, Metal, and Metal Oxide Particles on the Synthesis of Hydrochars

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ABSTRACT: Global concerns regarding climate change and the energy crisis have stimulated, among other things, research on renewable and sustainable materials. In relation to that, hydrothermal carbonization of wet biomass has been shown to be a low-cost method for the production of hydrochars. Such hydrochars can be refined into materials that can be used in water purification, for CO₂ capture, and in the energy sector. Here, we review the use of metal ions and particles to catalyze the formation of hydrochars and related hybrid materials. First, the effects of using silver, cobalt, tellurium, copper ions, and particles on the hydrothermal carbonization of simple sugars and biomass are discussed. Second, we discuss the structural effects of iron ions and particles on the hydrochars in conjunction with their catalytic effects on the carbonization. Among the catalysts, iron ions or oxides have low cost and allow magnetic features to be introduced in carbon-containing hybrid materials, which seems to be promising for commercial applications.

INTRODUCTION

The global warming, energy crisis, and various aspects of environmental pollution are concurrent critical issues. Aside from various policies and political measures, technological and scientific approaches are important to mediate the associated impact. Related research is focused on renewable energy sources such as solar, wind, and the use of sustainable and renewable resources. This review deals with recent developments in the use of metal ions and metal oxide particles for the synthesis of hydrochars, which can be derived from wet biomass in a cost- and energy-effective way.

Hydrochars are solid products formed during hydrothermal carbonization (HTC) of biomass or carbohydrates in aqueous media at usually 180–250 °C. This process was developed by Bergius as a way to imitate nature’s way to make coal and has recently been revisited using precursors such as xylose, glucose, fructose, ribose, furfural, and biomass such as coconut shells.

The formation of hydrochars is complex because of the multitude of simultaneous chemical reactions that occur during the hydrothermal treatment (Figure 1). Generally, the process first starts with the hydrolysis of saccharides into monomers, with glucose and fructose being the most abundant in lignocellulosic biomass. These molecules can then, under the hydrothermal conditions (set temperatures and self-generated pressures), decompose, dehydrate, and fragment, leading to the formation of smaller, condensed, and more reactive species. As glucose and fructose, as mentioned above, are the main constituents of lignocellulosic biomass, the result of these series of reactions are mainly hydroxymethylfurfural (HMF), furfural, as well as some aldehydes. These more reactive species undergo a series of cascade chemical reactions that include decomposition (to aldehydes, phenols, and organic acids) as well as polymerization, condensation (inter- and intramolecular), and aromatization reactions. These additive reactions ultimately form what is known as hydrochar.

There is no significant difference between the formation of hydrochar during HTC and that of humins in nature. As previously stated, HTC is a process designed from observing and mimicking nature. In studies done regarding the mechanism of formation of humins, it is thought that the tautomerization of glucose and fructose is of key importance for control in the formation of humins/hydrochar. Glucose must first tautomerize to fructose, which can then more readily dehydrate into HMF, a more reactive species as well as an important platform chemical in biorefinery processes.

The hydrochars obtained from HTC have been researched to be used as such for soil improvement and water treatment. Compared to biochars derived by pyrolysis, it can be argued that hydrochars possess some environmental advantages in relation to the thermodynamics and limited amounts of formed volatile organic compounds (VOCs) and CO₂, and they can be derived directly from wet biomass. Hydrochars can also be refined into...
activated carbons with applications in water purification and gas separation,9,10 superparamagnetic iron oxide particles can be included and give magnetic properties to the activated carbons.10

The chemical composition and molecular features of hydrochars have been studied with many methods, and in particular, multidimensional solid-state 13C NMR spectroscopy has been successful at revealing the detailed polymeric composition of hydrochars when prepared from glucose.11 As expected, the carbon content in hydrochars is positively affected by the temperature and time used for the HTC. When being prepared below a critical aromatization temperature, hydrochars are formed on the hydrothermal treatment. At long dwelling time and high temperature, the furanic rings undergo intermolecular condensation and decarboxylation, and the hydrochars obtain aromatic features.12 The hydrochars are also rich in carbonyl groups, and by increasing the temperature for the HTC, such functional groups are reduced in number. The morphological features of the hydrochar particles are very similar for such prepared from pure sugars and certain polysaccharides. For example, monodisperse hydrochar particles from HTC of sucrose are typically spheres.3 One possibility is that these spherical particles are being formed by phase-separated HMF and oligomers thereof, which are subsequently condensed; however, there are other possibilities of the formation of the spheres, and from our perspective, further detailed studies are needed.

## USE OF METAL IONS DURING HYDROTHERMAL CARBONIZATION

Bergius2 showed that various metal ions catalyzed the carbonization of sugars, and metal ions and particles affect the involved chemical reactions, which, in turn, impacts the structure, composition, and morphology of carbonaceous materials derived from hydrochars.13 Yu et al. demonstrated that the addition of dissolved AgNO3 led to the formation of fiber-like hydrochar structures, accelerated the HTC of starch, and increased the yield of the hydrochar.14 Yu et al. argued that Ag+ ions are reduced to Ag(0) nanoparticles by the reducing d-glucose obtained from the hydrolysis of starch. The Ag nanoparticles, in turn, catalyzed the carbonization reaction, and the yield increased from 18 to 54%.15 We argue that the HMF, furan, and aldehydes from the dehydration and decomposition of glucose were simultaneously polymerized around the nanoparticles that formed aggregated chains of particles. A gel-like layer of hydrochar was formed around the chains of Ag-based nanoparticles, which densified into a fiber-like structure by increasing the dwelling time of the reaction. As shown in Figure 2, some of the hydrochar fibers were partially filled with Ag particles. The formation rate for the Ag(0) nanoparticles and their associated concentration depended on the glucose concentration.15 As a result, the rate of reaction was controlled by the glucose concentration, which was deactivated into HMF and furfural and consumed during the HTC reaction.

In a comparative manner, Yu et al. used Cu(CH3COO)2 for the hydrothermal treatment of starch and obtained similar fibrous and hollow structures for the hydrochars.14 Cu2+ was reduced to Cu(0) nanoparticles by n-glucose, although Cu2+ has a lower reduction potential (E0 = 0.34 V) compared to that of Ag+(E0 = 0.8 V). The reason for the Cu2+ reduction can be attributed to increased redox potentials at high temperatures.16 The formation mechanism of the Cu-encapsulated hydrochars seemed to be similar to what was observed for the carbon fibers with encapsulated and aggregated Ag(0) nanoparticles. When Yu et al. studied the HTC of starch with dissolved Fe(NH4)2(SO4)2 and subsequently treated the hydrochars at 800 °C, they observed that hollow spheres of graphene had formed. It was highlighted that nanoparticles of Ag(0), Cu(0), and Fe(0) were involved in the alignment of the fiber-like hydrochars. In a related study, Chen et al. studied the effect of cobalt compounds on the HTC of furfural, and when Co(acac)2 was used, hydrochar particles with a flower-like structure were observed.17 They argued that the concurrent formation of CoO crystals was important to the morphology of the particles formed. Carbon-rich spheres were observed when Co(NO3)2 or CoCl2 were used. Co2+ has been shown to form clusters with furfural.18 We speculate that when the hydrothermal reaction proceeded, furfurals and HMF were aggregated into Co-acprecipitated CoO crystal structures of the spheres.17 It has been shown that...
during HTC of carbohydrates in the presence of cobalt compounds, Co(0), Co²⁺, and Co³⁺ ions coexist. Regarding biological and environmental applications, such as water purification and soil improvement, cobalt-treated hydrochars should be additionally treated for the removal of the cobalt compounds, which are toxic to biological systems.

HTC has been investigated as an approach for the synthesis of photoluminescent particles, using catalysts as in the study of Qian et al. They used tellurium-based nanowires and catalyzed the degradation of glucose and obtained fibers of hydrochars during HTC. The thin fibers were photoluminescent in the blue-violet spectrum and greater than 100 μm in length. By increasing the HTC temperature from 160 to 200 °C, the diameter of the fibers increased from 60 to 140 nm. Our interpretation of the involved chemistry indicates that tellurium forms an oxide layer in aqueous solutions, which then acts as a catalyst. We hypothesize that TeO₂ on the Te nanowires catalyzed the polymerization of HMF, furfural, and aldehydes into hydrochar fibers (Figure 4).

Tellurium-based compounds are toxic to the human biological system. Thus, the tellurium-treated hydrochars should be further processed for the removal of toxic compounds.

### EFFECT OF IRON IONS AND PARTICLES ON HYDROTHERMAL CARBONIZATION OF BIOMASS

#### Structural and Compositional Effect of Iron Ions and Iron Oxide Particles on the Formation of Hydrochar and Biooil

The effect of iron particles and ions on HTC of biomass and carbohydrates has attracted some attention. These particles and ions catalyze the formation of hydrochar and biooil and affect the structural and morphological features of the hydrochar. Moreover, iron is an inexpensive and abundant element and thus a suitable additive for the mass production of hydrochars and related materials. Hydrated Fe²⁺ and Fe³⁺ will acidify the aqueous solutions (pH 1–3). The acidity of iron-containing solutions is due to the positive charge of iron ions, which pulls electrons from the O–H bond of the H₂O in the first coordination shell, which, in turn, increases the tendency to release H⁺ to the solution. Polymerization of hydrochars by iron catalysis may follow the Cossee–Arlman mechanism by forming an iron complex with the organic matter. Acidic and hydroxyl groups from carboxylic acids and phenols act as an electron shuttle or redox mediator and drive the reduction pathway of (e⁻ + Fe³⁺ → Fe²⁺).

Cui et al. reported in a seminal study on the effect of [Fe(NH₄)₂(SO₄)₂] and iron oxide on HTC of starch and rice. The hydrochar consisted of spherical particles with diameters of about 2 μm (Figure 5), and as it has already been mentioned, spherical particles of hydrochar are commonly observed when glucose and related carbohydrates are used in the HTC.

Acids such as FeCl₃ have also been used for the synthesis of hydrochars in HTC since the time of Bergius. For example, Wang et al. reported the formation of a “dual-core Fe₂O₃@carbon structure” during HTC with water, FeCl₃, and chitosan. They observed a formation of Fe₂O₃ and proposed that the amine groups of chitosan chelated with Fe³⁺ on the Fe₂O₃ and that this chelation was involved in the formation of the iron/hydrochar structures. It is unclear to us if this mechanism holds at the end of the reaction as the primary amines of chitosan are likely decomposed during HTC.

Applications of Iron-Containing HTC Products in Water Treatment. Hydrochars can be used in different applications such as catalysis, water treatment, gas separation, etc. Iron-containing hydrochars are specifically attractive in the removal of heavy metals and volatile organic compounds.
from water because of their surface functional groups and magnetic features. Wang et al. used what they describe as dual-core Fe2O3@hydrochar structures for the adsorption of Cu2+ and Cr6+ from water. At a pH range of 2–5, the iron-oxide-containing carbon structures adsorbed Cr6+ (the highest adsorption at pH 2) and Cu2+ (the highest adsorption at pH 5).25

The release of pharmaceuticals into urban water systems and lakes is an emerging issue in relation to human health and the ecosystems. Yu et al. studied the removal of various types of estrogens at a pH range of 4–9 from water using a pyrolyzed iron/hydrochar composite.27 They pyrolyzed the hydrochar samples at 600 °C. The XPS results showed the coexistence of Fe2O3 and ferricydrate in the iron/hydrochar composite.

Transmission Electron Microscopy and Electron Energy Loss Spectroscopy Studies of Iron-Containing Hybrid Materials. Transmission electron microscopy (TEM) is a powerful characterization tool for metal and metal oxides in hydrochars and related carbon-based materials. High-resolution TEM and electron diffraction (ED) information can be used to identify mixed phases, solve crystal structures, and map out the nature of a complex multiphase system used in catalysts, for example. Energy-dispersive X-ray spectroscopy (EDX) and mapping techniques allow one to analyze the elemental composition of samples containing reasonably heavy elements. With electron energy loss spectroscopy (EELS), the spectra of the inelastically scattered electrons are recorded and images or diffraction patterns from electrons of a specific energy can be formed, interpreted, and quantified. EELS is well-suited to detect light elements, which are difficult to analyze with EDX. EELS offers more information than mere elemental identification; for example, it can be used as a very sensitive probe for the study of the oxide- and carbon-containing species in metal-supported carbon catalysts. High-angle annular dark-field or scanning transmission electron microscopy that provide atomic structure images with excellent atomic-number sensitivity can be used to determine the precise location and identity of individual atoms or clusters with sub-angstrom resolution in three dimensions.

Liu et al. reported the dispersion of Fe(0) on a hydrochar support. They first treated pinewood sawdust-derived hydrochars with Fe(NO3)3 at room temperature. Subsequently, the iron-impregnated hydrochars were heated at above 400 °C to obtain a pyrolyzed Fe(0)/carbon composite.28 Apart from showing the morphology of the sample, TEM images provided evidence that the Fe(0) particles were uniformly dispersed within the hydrochar matrix, in which the size of the Fe(0) particles could be measured. High-resolution TEM was applied to identify the crystalline graphitic carbon and the amorphous carbon as shown in Figure 6.

Janbroers et al. studied carbonized iron catalysts for Fischer–Tropsch synthesis by in situ TEM-EELS. The carbonized iron-based catalysts were composed of iron carbide and magnetite. The lattice spacings were observed at high magnification and were consistent with the d-spacings of hematite.29 Fourier transforms of the crystalline areas were performed to determine the lattice spacing of iron oxide and iron carbide so that these two species could be distinguished. They used the peak areas of the EELS edges to determine the valence states of the iron species and to calculate the iron/oxygen ratio, which is a semiquantitative way to determine the relative degree of oxidation. By calculating the L3/L2 area ratios from the EELS data, as shown in Figure 7, the oxidation state of the iron was determined. As a result, the L3/L2 ratios were found to be similar (5.7, 5.8, and 5.4) for the samples and the hematite reference, which proved that the iron in all samples was Fe(+3), which was consistent with the hematite structure. Jin et al. also applied the EELS technique on iron catalysts for Fischer–Tropsch synthesis and studied the Fe L2,3 edge, carbon K edge, and oxygen K edge structure of the samples.30 The EELS analyses could clearly differentiate between amorphous surface carbon and surface oxide films. They were therefore able to analyze the iron carbide particles covered with a surface layer of amorphous carbon and those with a surface layer of amorphous oxide. On the latter particles, they analyzed the carbon K edge related to the iron carbide phase. Using EELS, three different carbonaceous species, amorphous and graphitic carbon on the surface of carbide particles and carbide carbon, were clearly identified. In their previous study,31 the reactivity of these carbonaceous species was studied and related to the ease of hydrogenation of these carbonaceous species. The amorphous carbon which had been formed on the surface of the carbide particles was very reactive and could be readily hydrogenated in a flow of H2 at room temperature, whereas the graphitic carbon could only be hydrogenated at increased temperatures. The EELS results were of great interest and could be correlated with the observed reactivity of these carbonaceous species.
CONCLUSION

HTC of simple sugars and certain polysaccharides can be performed without the addition of metal ions or metal particles. However, metal ions, metal, or metal oxide particles influence the structure and composition of the hydrochars or metal-(oxide)−hydrochar hybrids and catalytically accelerate the involved hydrothermal reactions. In the review, we showed that the features and yields of the hydrochars could be changed with the addition of metal ions or metal oxide particles. In particular, we highlighted the effect of the use of iron, in various forms, during the HTC. Iron is a low-cost element and has catalytic and structural effects on the HTC products. In the review process, we learned that the acidic Fe²⁺ and Fe³⁺ could complex with HMF, furan, and aldehydes, which can further decompose and polymerize into hydrochars. However, the mechanistic models which have been proposed for the reaction pathway of iron-treated hydrochars are not very well elaborated. Further studies in real time of the chemical reactions during HTC could enhance the understandings of the hydrothermal reaction pathways with Fe²⁺ and Fe³⁺ being present. With such pathways being resolved, it could be more straightforward to derive iron oxide−hydrochar hybrid materials for defined applications and further refinements.

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Notes
The authors declare no competing financial interest.

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Vahid Saadattalab received his B.S in Applied Chemistry from University of Tabriz, Iran, in 2013. He completed his M.S studies at the University of Tehran in 2017 while he was a member of nanoparticles and coatings laboratory (NCL) working on solar cells. He is currently a Ph.D. student in Niklas Hedin’s group in the Department of Materials and Environmental Chemistry (MMK) at Stockholm University and works on hydrothermal carbonization of biomass.

Anthony Edward Szego obtained a B.Sc. in Chemistry from the University of Seville, period of time during which he discovered his interest in the application of catalysis as well as the importance of applying new technologies in the context of climate change. This led him to enrol and complete a Master’s Degree in Catalysis from Cardiff University. After finishing his M.Sc., he was selected to partake with a Marie Curie scholarship in the Green Carbon group with which he is currently working since 2018 at Stockholm University in Niklas Hedin’s research group in the Department of Materials and Environmental Chemistry.

Xia Wang started her Ph.D. studies with Niklas Hedin in June 2017. Her research is about refining carbons using templating techniques and studying their applications. Recent focus is on the colloidal chemistry of carbon particles. She often uses transmission electron microscopy and has just started to learn electron energy loss spectroscopy.
Niklas Hedin, Ph.D., from the Royal Institute of Technology in Physical Chemistry, Stockholm, with István Fűró. Postdoctoral research with Bradley Chmelka at the University of California at Santa Barbara and with Sebastian Reyes at ExxonMobil Corporate Research Laboratory, Annandale, US. Now Professor of Materials Chemistry at Stockholm University, Sweden. Current focus on adsorbents for separation or reduction of carbon dioxide and carbon materials derived by hydrothermal carbonization. A multimethod approach is applied.

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**REFERENCES**

(1) Zhang, Z.; Zhu, Z.; Shen, B.; Liu, L. Insights into Biochar and Hydrochar Production and Applications: A Review. Energy 2019, 171, 581–598.

(2) Bergius, F. C. R. Die Anwendung Hoher Drucke Bei Chemischen Vorgängen Und Eine Nachbildung Des Entstehungsprozesses Der Steinkohle; W. Knapp, 1913.

(3) Wang, Q.; Li, H.; Chen, L.; Huang, X. Monodispersed Hard Carbon Spherules with Uniform Nanopores. Carbon 2001, 39, 2211–2214.

(4) Titirici, M. M.; White, R. J.; Falco, C.; Sevilla, M. Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage. Energy Environ. Sci. 2012, 5, 6796.

(5) Antal, M. J.; Mok, W. S. L.; Richards, G. N. Mechanism of Formation of S-(Hydroxymethyl)-2-Furaldehyde from d-Fructose and Sucrose. Carbohydr. Res. 1990, 199, 91–109.

(6) Tslomoleikis, G.; Orella, M. J.; Lin, Z.; Cheng, Z.; Zheng, W.; Nikolakis, V.; Vlachos, D. G. Molecular Structure, Morphology and Growth Mechanisms and Rates of S-Hydroxymethyl Furural (HF) Derived Humins. Green Chem. 2016, 18, 1983–1993.

(7) Abel, S.; Peters, A.; Trinks, S.; Schonsky, H.; Facklam, M.; Wessolek, G. Impact of Biochar and Hydrochar Addition on Water Retention and Water Repellency of Sandy Soil. Geoderma 2013, 202–203, 183–191.

(8) Yang, D. P.; Li, Z.; Liu, M.; Zhang, X.; Chen, Y.; Xue, H.; Ye, E.; Luque, R. Biomass-Derived Carbonaceous Materials: Recent Progress in Synthetic Approaches, Advantages, and Applications. ACS Sustainable Chem. Eng. 2019, 7, 4564–4585.

(9) Rodríguez Correa, C.; Ngamying, C.; Klank, D.; Kruse, A. Investigation of the Textural and Adsorption Properties of Activated Carbon from HTCC and Pyrolysis Carbonizates. Biomass Convers. Biorefin. 2018, 8, 317–328.

(10) Hao, W.; Björkman, E.; Yun, Y.; Lilliestræle, M.; Hedin, N. Iron Oxide Nanoparticles Embedded in Activated Carbons Prepared from Hydrothermally Treated Waste Biomass. ChemSusChem 2014, 7, 875–882.

(11) Falco, C.; Perez Caballero, F.; Babonneau, F.; Gervais, C.; Laurent, G.; Titirici, M. M.; Baccile, N. Hydrothermal Carbon from Biomass: Structural Differences between Hydrothermal and Pyrolyzed Carbons via 13C Solid State NMR. Langmuir 2011, 27, 14460–14471.

(12) Sevilla, M.; Fuertes, A. B. Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides. Chem. - Eur. J. 2009, 15, 4195–4203.

(13) Cui, X.; Antonietti, M.; Yu, S. H. Structural Effects of Iron Oxide Nanoparticles and Iron Ions on the Hydrothermal Carbonization of Starch and Rice Carbohydrates. Small 2006, 2, 756–759.

(14) Yu, S. H.; Cui, X. J.; Li, L. L.; Li, K.; Yu, B.; Antonietti, M.; Colfen, H. From Starch to Metal/Carbon Hybrid Nanostructures: Hydrothermal Metal-Catalyzed Carbonization. Adv. Mater. 2004, 16, 1636–1640.

(15) Baksi, A.; Gandi, M.; Chaudhari, S.; Bag, S.; Gupta, S. S.; Pradeep, T. Extraction of Silver by Glycine. Angew. Chem., Int. Ed. 2016, 55, 7777–7781.

(16) Salz, D.; Mahltig, B.; Baalmann, A.; Wark, M.; Jaeger, N. Metal Clusters in Plasma Polymer Matrices. Part III. Optical Properties and Redox Behaviour of Cu Clusters. Phys. Chem. Chem. Phys. 2000, 2, 3105–3110.

(17) Chen, X.; Li, X.; Liu, S.; Li, Z. Effects of Cobalt Compounds on the Morphology and Structure of Carbonaceous Materials Prepared by Hydrothermal/Solvothermal Carbonization of Furfural. Ind. Eng. Chem. Res. 2015, 54, 4756–4762.

(18) Dianzhong, F.; Bo, W. Complexes of Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Manganese(II) with Tridentate Schiff Base Ligand. Transition Met. Chem. 1993, 18, 101–103.

(19) Li, X. L.; Zhang, K.; Chen, S. Y.; Li, C.; Li, F.; Xu, H. J.; Fu, Y. A Cobalt Catalyst for Reductive Eutherification of 5-Hydroxymethyl-Furfural to 2,5-Bis(Methoxyethyl)Furan under Mild Conditions. Green Chem. 2018, 20, 1095–1105.

(20) Sekizawa, J. Concise International Chemical Assessment Document (CICAD): A New Chemical Safety Series in IPCS, Internationalizing National Reviews. Eisai Shikenjo Hokoku 1996, 114, 89–94.

(21) Qian, H. S.; Yu, S. H.; Luo, L. B.; Gong, J. Y.; Fei, L. F.; Liu, X. M. Synthesis of Uniform Tg@Carbon-Rich Composite Nanocables with Photoluminescence Properties and Carbonaceous Nanofibers by the Hydrothermal Carbonization of Glucose. Chem. Mater. 2006, 18, 2102–2108.

(22) Cerwenka, E. A.; Cooper, W. C. Toxicology of Selenium and Tellurium and Their Compounds. Arch. Environ. Health 1961, 3 (2), 189–200.

(23) Cossee, P. Ziegler-Natta catalysis I. Mechanism of Polymerization of α,α'-Olefinos with Ziegler-Natta Catalysts. J. Catal. 1964, 3, 80–88.

(24) Vindedahl, A. M.; Strehlah, J. H.; Arnold, W. A.; Penn, R. L. Organic Matter and Iron Oxide Nanoparticles: Aggregation, Interactions, and Reactivity. Environ. Sci. Nano 2016, 3, 494–505.

(25) Wang, X.; Zhan, C.; Ding, Y.; Ding, B.; Xu, Y.; Liu, S.; Dong, H. Dual-Core Fe2O3@Carbon Structure Derived from Hydrothermal Carbonization of Chitosan as a Highly Efficient Material for Selective Adsorption. ACS Sustainable Chem. Eng. 2017, 5, 1457–1467.

(26) Yang, Y.; Cui, J.; Zheng, M.; Hu, C.; Tan, S.; Xiao, Y.; Yang, Q.; Liu, Y. One-Step Synthesis of Amino-Functionalized Fluorescent Carbon Nanoparticles by Hydrothermal Carbonization of Chitosan. Chem. Commun. 2012, 48, 380–382.

(27) Yu, J.; Zhu, Z.; Zhang, H.; Chen, T.; Qiu, Y.; Xu, Z.; Yin, D. Efficient Removal of Several Estrogens in Water by Fe-Hydrochar Composite and Related Interactive Effect Mechanism of H2O2 and Iron with Persistent Free Radicals from Hydrochar of Pinewood. Sci. Total Environ. 2019, 658, 1013–1022.

(28) Liu, Z.; Zhang, F.; Hoekman, S. K.; Liu, T.; Gai, C.; Peng, N. Homogeneously Dispersed Zerovalent Iron Nanoparticles Supported
on Hydrochar-Derived Porous Carbon: Simple, in Situ Synthesis and Use for Dechlorination of PCBs. *ACS Sustainable Chem. Eng.* 2016, 4, 3261−3267.

(29) Janbroers, S.; Louwen, J. N.; Zandbergen, H. W.; Kooyman, P. J. Insights into the Nature of Iron-Based Fischer−Tropsch Catalysts from Quasi in Situ TEM-EELS and XRD. *J. Catal.* 2009, 268, 235−242.

(30) Jin, Y.; Xu, H.; Datye, A. K. Electron Energy Loss Spectroscopy-(EELS) of Iron Fischer−Tropsch Catalysts. *Microsc. Microanal.* 2006, 12, 124−134.

(31) Jackson, N. B.; Datye, A. K.; Mansker, L.; O’Brien, R. J.; Davis, B. H. Deactivation and Attrition of Iron Catalysts in Synthesis Gas. In *Stud. Surf. Sci. Catal.* 1997; Vol. 111, pp 501−516. DOI: 10.1016/S0167-2991(97)80194-2.