ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

A Sustainable Approach for the Synthesis of Catalytically Active Peroxidase-Mimic ZnS Catalysts

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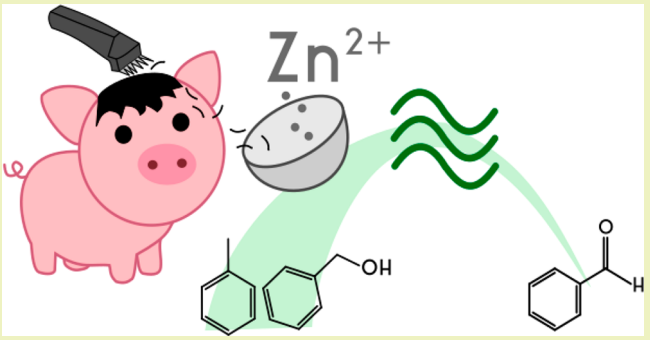
Supporting Information

ABSTRACT: Zinc sulfides are emerging as promising catalysts in different fields such as photochemistry or organic synthesis. Nevertheless, the synthesis of ZnS compounds normally requires the utilization of toxic sulfur precursors, e.g., thiourea which is a contaminant and carcinogenic agent. As a result, new green and sustainable synthetic methodologies are needed. Herein, an innovative, simple, and cheap approach for the synthesis of ZnS carbon composites is reported. Zinc acetate dihydrate was employed as metal precursor while wasted pig bristles were employed as carbon and sulfur source. The phase and the morphology of the compounds were analyzed by XRD, XPS, SEM, and EDX and the surface area was determined by nitrogen physisorption. ZnS carbon materials showed remarkable peroxidase-like catalytic activity for two different model reactions: the liquid-phase selective oxidation of benzyl alcohol and toluene to benzaldehyde (conversions up to 63% and 29% and selectivities up to 86% and 87%, respectively) using hydrogen peroxide as oxidant under microwave irradiation.



KEYWORDS: *Zinc sulfide, Pig bristles, Microwave chemistry, Selective oxidations*

INTRODUCTION

Zinc sulfide has been studied as an important compound due to its unique physical and photochemical properties.[1−3] It has demonstrated an extraordinary versatility and potentiality for different applications including light-emitting diodes (LEDs), electroluminescence, infrared windows, sensors, lasers, and biodevices.[4−6] Additionally, ZnS possesses many interesting characteristics such as excellent transport properties, an intrinsically *n*-type semiconductivity, good thermal stability, high electronic mobility, nontoxicity, water insolubility, and low-production costs.[4−7]

All reported synthetic protocols for ZnS preparation involve the utilization of highly toxic sulfur sources including extremely hazardous compounds such as H_2S, or Na_2S as well as thioureas, highly contaminant and carcinogenic agents.[8−10] New green and low-toxicity sulfur sources are therefore required for sustainable development. In this context, pig bristles represent a cheap and largely available source of sulfur (and carbon). Pig bristles are considered as a waste toxic-free feedstock, easily collectable and accessible at industrial scale. In fact, ca. ∼225k tons of wasted pig bristles are yearly produced only in European slaughterhouses.[11] However, only a few works to date are available on the reutilization/use of pig bristles as food fodder supplements, while their valorization as chemical source is extremely limited.[11−13]

Herein, a simple and innovative synthesis of ZnS carbon composites derived from wasted pig bristles is reported. The synthetic procedure involved a facile heating step in a diluted aqueous solution of potassium hydroxide. Wasted pig bristles were employed as sulfur and carbon source while zinc acetate dihydrate was used as metal source. The material was characterized by XPS, XRD, N_2 physisorption, SEM, and EDX, demonstrating the successful formation of zinc sulfides carbon compounds.

In order to validate the practical application of the new material, ZnS carbon composites were tested as catalysts in two different model reactions: the selective oxidation of benzyl alcohol and toluene to benzaldehyde. Among all known oxidative transformations, the selective oxidations of alcohols to the corresponding carbonyl compounds have gained attention due to their broad range of industrial applications.[14,15] Specifically, the conversion of benzyl alcohol to benzaldehyde has attracted significant interest since benzaldehyde is a widely used chemical in food, pharmaceutical, and perfumery industries as well as building block in other chemical industries.[16−22] For example, benzaldehyde is commonly used as a flavor and fragrance agent tasting of

Received: September 27, 2018
Revised: November 5, 2018
Published: December 7, 2018

DOI: 10.1021/acssuschemeng.8b04968
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

almond, peach, marzipan, and pistachio. In addition, benzaldehyde can be also synthesized via toluene oxidation.[23] Considering that toluene is classified as a highly pollutant chemical, its oxidation to beneficial chemicals products, i.e., benzyl alcohol, benzaldehyde, benzoic acid, and benzoate, is extremely attractive.[24,25] For example, benzoic acid is industrially obtained from toluene using (thermally driven) Co-based catalyzed reactions.[26]

ZnS carbon compounds were particularly tested in fast microwave-assisted reactions, using only hydrogen peroxide as oxidant. Less aggressive oxidants such as hydrogen peroxide (H_2O_2) and molecular oxygen (O_2) are nowadays employed aiming to scale up oxidation processes,[14] whereas, in the past, the scale up of the oxidation reactions has been very limited due to the use of heavy metals (e.g., chromium, manganese, and permanganate derivatives).[27−30] In addition, the utilization of hydrogen peroxide allows the minimization of chemical waste in these catalytic processes, as water is the only reaction side product.

MATERIALS AND METHODS

Materials. Zinc acetate dihydrate ($Zn(CH_3COOH)_2{\cdot}2H_2O$), potassium hydroxide (KOH), acetone (CH_3COCH_3), ethanol (CH_3CH_2OH, 99.8%), acetonitrile (CH_3CN, 99.8%), benzyl alcohol ($C_6H_5CH_2OH$, 99.8%), toluene (C_7H_8, 99.8%), and hydrogen peroxide (H_2O_2, 30% v/v) were purchased from Sigma-Aldrich Inc., St. Louis, MO, USA. All reagents were used without any further purification.

Synthesis of ZnS Carbon Catalysts. A sequence of three ZnS carbon structures characterized by different synthesis times were prepared. In a typical procedure, the correct amount of zinc acetate dihydrate (850 mg, 3.8 mmol) was dissolved in 200 mL of 1.0 M KOH solution in a 250 mL round flask equipped with a stirring bar and a reflux condenser. Sequentially, 1.5 g of pig bristles (cut in pieces of ∼5 mm) was added. The mixture was kept at room temperature under vigorous magnetic stirring (800 rpm) for 10 min before starting the reaction. The mixture was then heated at reflux in an oil bath. After completing the reaction, the solution was naturally cooled down to r.t. and the light-brown precipitate was filtrated and washed several times with acetone and ethanol. Finally, the material was oven-dried at 100 °C for 24 h. Three different samples were produced by setting the heating time for 1 h, 3 h, and 5 h. The samples were denoted ZnS-1h, ZnS-3h, and ZnS-5h, respectively.

Material Characterization. ZnS carbon composites were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), powder X-ray diffraction (XRD), N_2 physisorption, and X-ray photoelectronic spectroscopy (XPS).

Scanning electron microscopy images were recorded with a JEOL JSM-6300 scanning microscope (JEOL Ltd., Peabody, MA, USA) equipped with energy-dispersive X-ray spectroscopy (EDX) of 15 kV at the Research Support Service Center (SCAI) from University of Cordoba.

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 DISCOVER A25 diffractometer (PanAnalytic/Philips, Lelyweg, Almelo, The Netherlands) using Cu Kα (λ = 1.5418 Å) radiation. Wide angle scanning patterns were collected over a 2θ range from 10° to 80° with a step size of 0.018° and counting time of 5 s per step.

Textural properties of the samples were determined by N_2 physisorption using a Micromeritics ASAP 2020 automated system (Micromeritics Instrument Corporation, Norcross, GA, USA) with the Brunauer−Emmet−Teller (BET) and the Barrett−Joyner−Halenda (BJH) methods. Prior to analysis, the samples were outgassed for 24 h at 100 °C under vacuum (P_0 = 10^{-2} Pa) and subsequently analyzed.

XPS studies were performed at the Central Service of Research Support (SCAI) of the University of Cordoba, using an ultrahigh vacuum (UHV) multipurpose surface analysis system Specs. The experiments were carried out at pressures < 10^{-10} mbar, using a conventional X-ray source (XR-50, Specs, Mg-Kα, $h\nu$ = 1253.6 eV, 1 eV = 1.603 × 10^{-19} J) in a "stop and go" mode. The samples were deposited on a sample holder using a double sided adhesive tape, and afterward evacuated overnight under vacuum (<10^{-6} mbar). Spectra were collected at room temperature (pass energy: 25 and 10 eV, step size: 1 and 0.1 eV) with a Phoibos 150-MCD energy detector. The deconvolutions of the obtained curves and element quantification were carried out using XPS CASA program.

Catalytic Activity. The oxidation tests were performed following a procedure optimized in a previous work.[31] Briefly, 25 mg of catalyst, 0.1 mL of benzyl alcohol (0.95 mmol) or 0.1 mL of toluene (0.94 mmol), 0.25 mL of hydrogen peroxide (30% v/v), and 2 mL of acetonitrile as solvent. Blank tests were run in the absence of the catalysts. Both microwave-assisted oxidations were carried out in a CEM-Discover microwave reactor, equipped with a PC-controlled interface. The mixtures were irradiated for 45 min, withdrawing aliquots for GC-FID analysis every 15 min. The experiments were performed in closed vessels. The "discover" method was used under pressure, allowing the control of the irradiation power, the temperature, and the pressure. The reactions were stirred and heated with microwave irradiation, fixing the temperature at 120 °C by an infrared probe. The autogenous pressure ranged from 3.5 to 8 bar.

Product Analysis. The filtrates collected from the reaction mixtures were analyzed by GC, using an Agilent 19091J-413 GC model equipped with a Supelco 2-8047-U (30 m × 0.32 mm × 0.25 μm i.d.) capillary column and an FID detector. The temperature of the column was ramped at 25 °C min^{-1} to 25 °C (1 min hold time), then at 25 °C min^{-1} to 250 °C (5 min hold time), and finally to 300 °C at 20 °C min^{-1} (10 min hold time). The nitrogen gas flow was set at 1.3 mL min^{-1}.

RESULTS AND DISCUSSION

Synthesis of ZnS Carbon Composites. A simple, fast, and cheap methodology is shown for the synthesis of ZnS carbon structures using wasted pig bristles as carbon and sulfur source. As reported by Gonzalo et al., pig bristles are carbon- and sulfur-rich wastes largely produced in most industrialized countries, generally burnt as waste or partially reused in brush industries or as food fodder supplement.[12,13,32] The sulfur contained in pig bristles is mainly derived from keratin, an insoluble protein containing disulfide bonds as well as from amino acids such as cysteine, methionine, and cysteic acid.[33] Due to similarities with human hair, the total amount of sulfur contained in pig bristles has been reported to be ca. 5% wt.[34] However, contrary to human hair, which production is also vast but distributed in the numerous barber shops, pig bristles are produced in large quantities in slaughterhouses and can be easily collected at industrial scale.

As illustrated in Figure 1, the new synthesis involved a unique step where a mixture of pig bristles, zinc acetate

Figure 1. Schematic illustration of the preparation of ZnS.

dihydrate, and a solution 1.0 M of potassium hydroxide was heated up under reflux conditions.

The synthesis is adapted from a previously reported protocol for the preparation of Cu_2S, where the solvent solution, made of ethylene glycol and NaOH, has been substituted with a less hazardous and easier to manipulate dilute aqueous solution of KOH.[11] Ethylene glycol is indeed a suspicious carcinogenic

DOI: 10.1021/acssuschemeng.8b04968
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

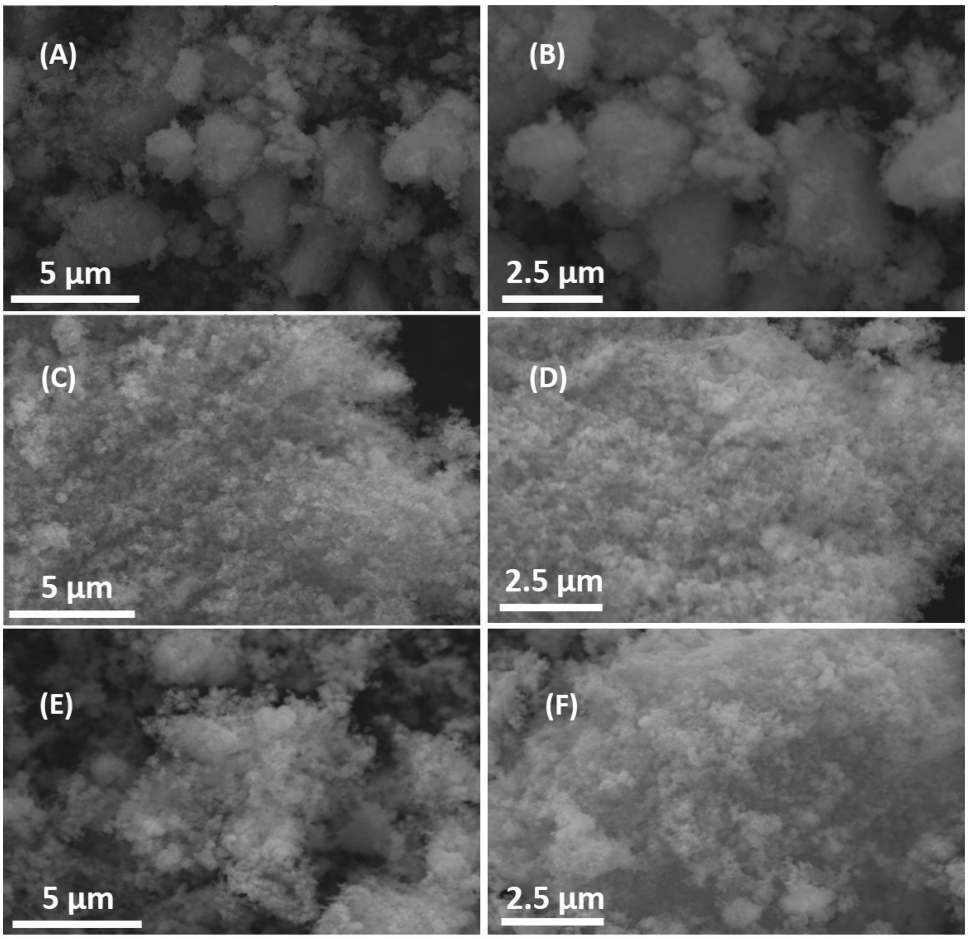


Figure 2. SEM images of the three different ZnS composites. (A, B) ZnS-1h; (C, D) ZnS-3h; (E, F) ZnS-5h.

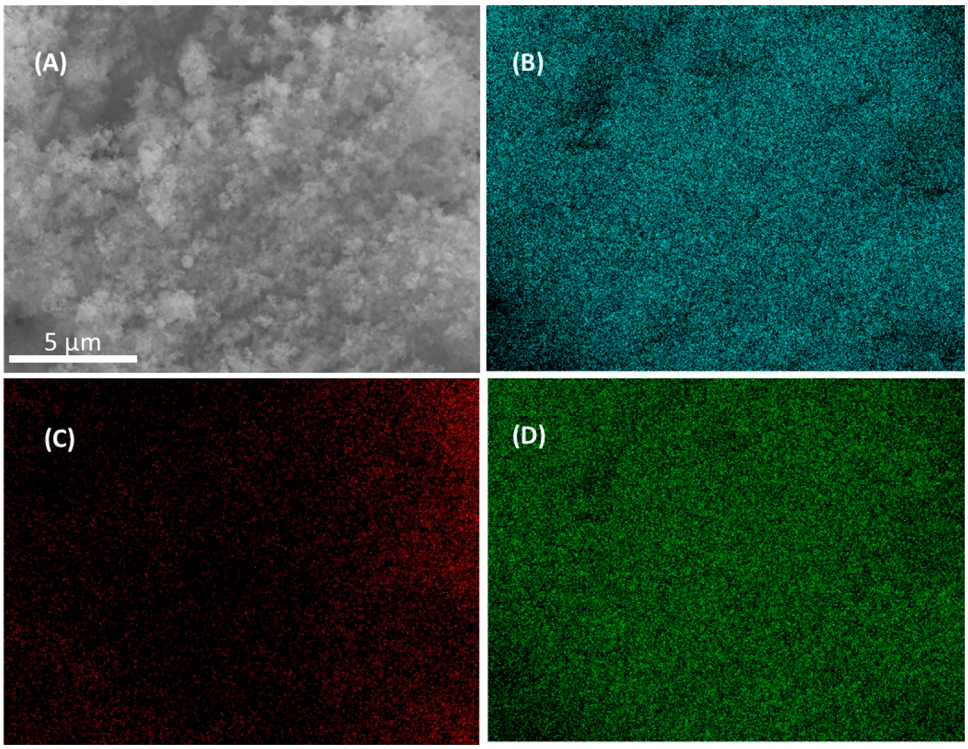


Figure 3. SEM images of ZnS-3h with mapping analysis of (A) ZnS carbon structure, (B) zinc, (C) carbon, and (D) sulfur.

DOI: 10.1021/acssuschemeng.8b04968
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

agent and can explosively degrade when heated up with NaOH. The aqueous basic solution of KOH was employed in order to accelerate and facilitate the decomposition of pig bristles and the release of sulfur via keratin hydrolysis.[35] Without the basic solution, the thermal degradation would require higher temperature and processing time. In fact, keratin and amino acids present in proteins start to thermally degrade above 150 °C, and release sulfur up to 300 °C.[36]

When the mixture was heated up, the pig bristles started to decompose and the dissolved Zn^{2+} ions bind with sulfur. During this step, the particles self-aggregate in order to minimize the surface energy, incorporating the residual carbon, and forming homogeneous ZnS carbon structures. Three different samples were prepared, using the same amount of pig bristles and zinc acetate dihydrate and heating up the reaction mixture for different times, respectively 1 h, 3 h, and 5 h. The zinc sulfide carbon materials were denoted as ZnS-1h, ZnS-3h, and ZnS-5h.

Materials Characterization. The morphology of ZnS carbon structures was investigated by SEM and EDX analyses. Figure 2 shows SEM images for the three ZnS carbon materials. All samples exhibited a "coral-like" homogeneous morphology where the carbon derived from the degradation of pig bristles was aggregated with ZnS. EDX mappings were reported in order to demonstrate the distribution of catalytically active sites, as reported in Figure 3 for sample ZnS-3h.[37] Remarkably, zinc, sulfur, and carbon were found to be well distributed in the material, confirming the homogeneous conditions of the synthesis, and the presence of active sites over all the catalyst surface (please see Figures S1 and S2 for ZnS-1h and ZnS-5h EDX mapping).

EDX-mapping micrographs showed the presence of carbon, sulfur, and zinc, indicating the high purity of the materials. The phase purity and crystallinity of synthesized ZnS carbon composites were subsequently investigated by XRD analysis. As shown in Figure 4, XRD patterns for all different samples showed the presence of zinc sulfide. The diffraction peaks at 29.04°, 48.38°, and 57.42° could be indexed to the (1 1 1), (2 2 0), and (3 1 1) planes of cubic zinc sulfide (JCPDS 01-080-0020).[38] No other impurity peaks detected through XRD also suggested high purity in the materials. In addition, the width of the most intense peaks at half height measured almost the same for the three patterns, indicating similar dimensions of the particles in all the samples, according to Scherrer's equation.[39]

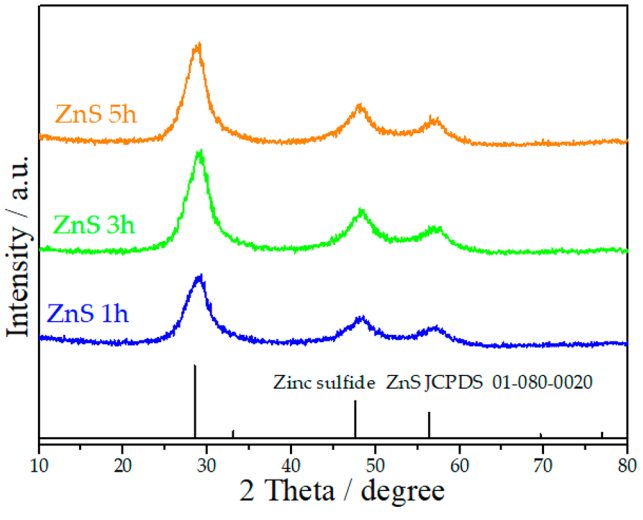


Figure 4. XRD patterns for ZnS carbon composites.

The samples were thus subjected to an XPS study. Figure 5 shows plots of high-resolution spectra concerning C 1s, Zn 2p, and S 2p regions. A summary of the fitting position values for the different elements mentioned as well as the surface atomic ratios (C/Zn) is presented in Table 1. In agreement with XRD analysis, the presence of a defined ZnS structure was successfully observed for all synthesized ZnS materials. In particular, both Zn 2p and S 2p core level spectra do not display significant modifications with synthesis time (middle and right panels of Figure 5). Zn 2p shows two strong peaks at ca. 1021.5 and 1044.8 eV, assigned to the binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, indicating the existence of Zn(II) and discarding the possible presence of oxidized minority species.[40,41] The value of ca. 161.2 eV is in good agreement with the S $2p_{3/2}$ typical value for ZnS.[40] In contrast, a significant difference can be observed for C 1s XPS region. All samples show the dominant typical C-C contribution at 284.6 eV (C2) corresponding to adventitious C. However, certain differences were detected for the other C-related species as can be seen in the left panel of Figure 5 and Table 1. Carbon species evolve over the time of synthesis. The contribution located around 287 eV (C1), typically attributed to C-O, shifts to less binding energy when higher reaction times were used. The evolution of carbon species is even more evident for the contribution situated at less energy with respect to the C−C bond (C3). These unexpected contributions were detected at 281.2 and 279.9 for ZnS-1h and ZnS-3h, respectively, and could be associated with an interaction between C and Zn species. The detected modifications of carbon-related species on the surface of ZnS have also a certain influence on the final carbon content of the samples. C/Zn ratio indicated that cleaner carbon samples can be obtained using longer reaction times. This fact had a relative influence on the final catalytic properties through the series as discussed in further sections.

Physisorption experiments were carried out in order to determine the specific surface area of the materials by nitrogen adsorption−desorption measurements. The samples were observed to be low porous materials with surface areas of 50 m^2/g, 53 m^2/g, and 57 m^2/g for ZnS-1h, ZnS-3h, and ZnS-5h, respectively. The so-obtained values showed a linear and small increment of the surface area increasing the reaction time. This relation can be correlated to the lower content of carbon observed in XPS analysis (Table 1). In addition, the values obtained for samples ZnS-1h and ZnS-3h were similar, in good agreement with the stabilization of carbon species described in XPS analysis. The maximum value obtained for ZnS-5h confirmed the production of a material with more active sites on the surface.

Catalytic Activity. The catalytic activity of the materials has been investigated in two different reactions: the selective liquid-phase oxidation of benzyl alcohol and toluene to benzaldehyde. ZnS has been recently demonstrated to exhibit peroxidase-like activities for the degradation of H_2O_2 into hydroxyl radicals (·OH), which act as oxidants for toluene and benzyl alcohol.[42] The reported mechanism for the oxidation of toluene **1** and benzyl alcohol **2** to benzaldehyde **3** is illustrated in Scheme 1.[43] The only detectable side product of the reaction was benzoic acid **4**. No other products were detected.

DOI: 10.1021/acssuschemeng.8b04968
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

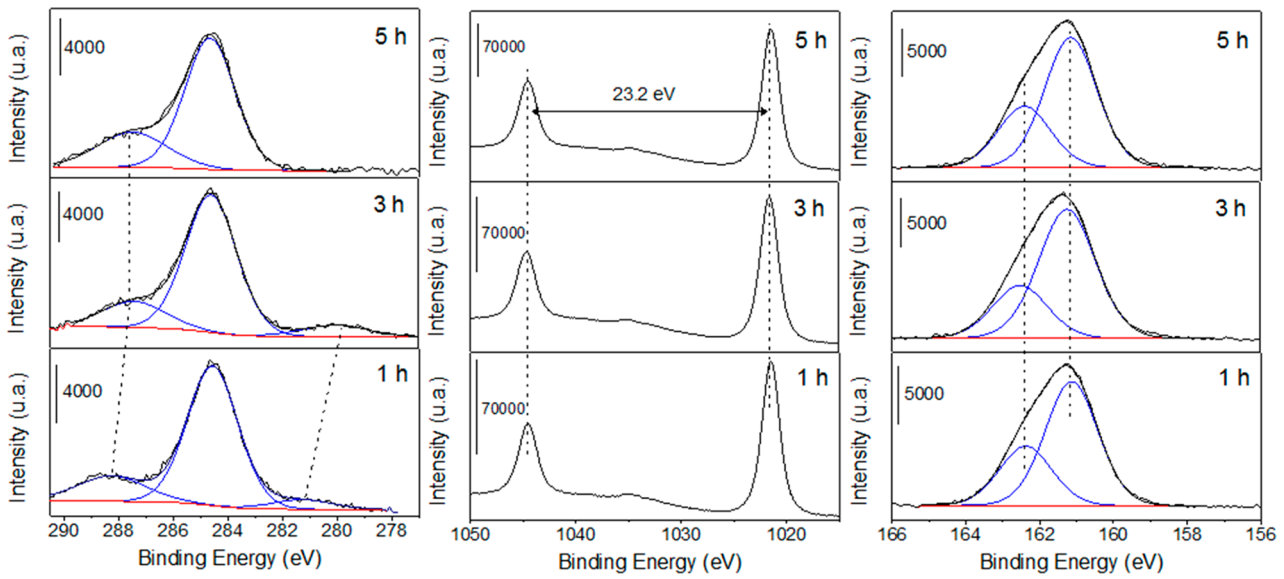


Figure 5. XPS patterns for ZnS carbon composites.

Table 1. XPS Data for ZnS Samples

	position					
			C 1s (eV)			
sample	Zn $2p_{3/2}$ (eV)	S $2p_{3/2}$ (eV)	C1	C2	C3	C/Zn
ZnS-1h	1021.5	161.1	288.3	284.6	281.2	3.6
Zns-3h	1021.6	161.2	287.4	284.6	279.9	3.5
ZnS-5h	1021.5	161.2	287.5	284.6		2.2

The results were confirmed by a carbon balance (>95% in all tests).

The oxidation reaction of benzyl alcohol was carried out using the three ZnS carbon composites as heterogeneous catalysts. Results reported in Table 2 show that conversions observed were ca. ~60−65% for all ZnS carbon materials after 15 min of microwave irradiation. Within the same time, the selectivity was observed to be 70%, 85%, and 87% for samples ZnS-1h, ZnS-3h, and ZnS-5h, respectively. In terms of conversion, an increase of the reaction time to 30 and 45 min did not have any influence in reaction yields. Most importantly, the selectivity dropped to 64% for ZnS-1h, 82% for ZnS-3h, and 84% for ZnS-5h. On the basis of these data, all catalysts exhibited an almost identical conversion while the best selectivity was observed after 15 min employing ZnS-5h catalyst, most probably due to the larger surface area (57 g/m^2 vs 50 g/m^2 of ZnS-1h). Hypothetically, the higher surface area facilitated the rapid decomposition of H_2O_2 into hydroxyl radicals, which directly oxidized benzyl alcohol. A lower surface area (ZnS-1h) would have taken more time to decompose hydrogen peroxide; therefore, more benzyl alcohol could have been already oxidized to benzaldehyde and sequentially to benzoic acid, reducing the selectivity. In addition, sample ZnS-5h exhibited a lower C/Zn surface ratio, indicating that more active zinc sulfide sites were accessible for the degradation of hydrogen peroxide using this catalyst.

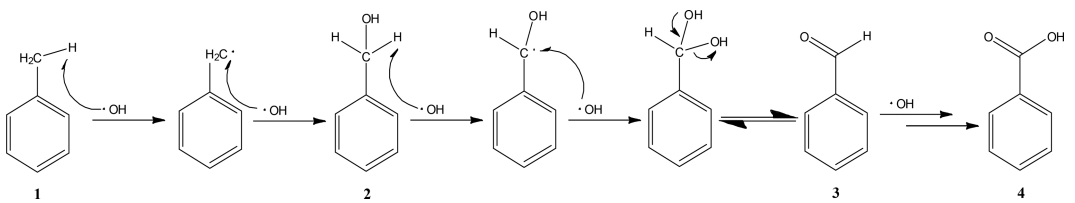
The stability of the catalysts was studied using the most active material ZnS-5h. The catalyst was reused up to 4 times, and the activity and selectivity to benzyl aldehyde was found to be almost identical to that of the fresh catalyst as shown in Figure 6 (for the numeric data, please see Table S1).

The results of the oxidation of toluene to benzaldehyde are reported in Table 3. After 15 min of reaction, the best result was obtained with ZnS-5h (19%), while the selectivity was approximately the same value (around 90%) for all three zinc sulfide carbon materials. After 30 min, an increase of conversion up to 29% with ZnS-5h was observed, while the conversion with ZnS-1h and ZnS-3h remained unchanged. On the other hand, the selectivity did not improve for any catalyst. After 45 min, the values of conversion and selectivity were equal to those obtained after 30 min, confirming that the reaction was not proceeding.

On the basis of these considerations, the most active catalyst was ZnS-5h, which again showed the best results after 30 min reaction. Such optimum behavior could be again explained in terms of the higher surface area and higher Zn/C ratio for ZnS-5h.

The stability tests were carried out using ZnS-5h. The catalyst was reused up to 4 times without any appreciable losses of activity or selectivity to benzaldehyde, as shown in Figure 7.

Scheme 1. Proposed Mechanism for Toluene and Benzyl Alcohol Oxidation



DOI: 10.1021/acssuschemeng.8b04968
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Table 2. Conversion and Selectivity Results for the Oxidation of Benzyl Alcohol

	15 min		30 min		45 min	
sample	conversion/%	selectivity/%	conversion/%	selectivity/%	conversion/%	selectivity/%
BLANK	<15	55.4	<15	53.8	<15	52.1
ZnS-1h	63.0	70.2	63.8	65.0	64.0	64.1
ZnS-3h	62.6	85.1	62.7	83.2	63.0	82.1
ZnS-5h	62.7	87.1	63.1	85.8	63.4	84.3

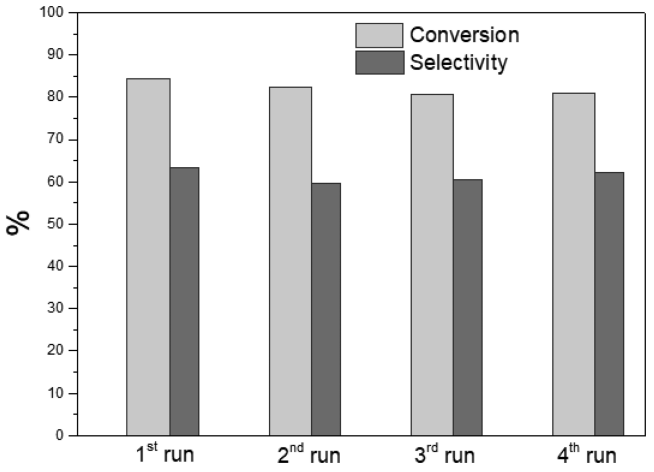

Figure 6. Schematic representation of conversion and selectivity of the most active catalyst up to the 4th run of the oxidation of benzyl alcohol.

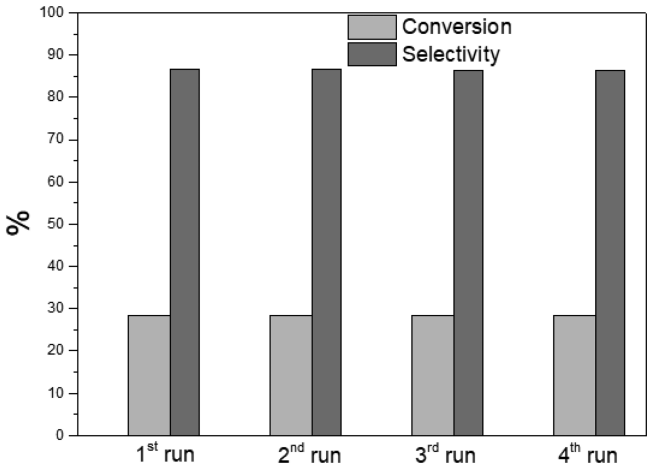

Figure 7. Schematic representation of conversion and selectivity to benzyl aldehyde for the most active catalyst up to 4th run for the oxidation of toluene (for the numeric data, please see Table S2).

CONCLUSIONS

A simple, effective, and sustainable methodology has been reported for the preparation of ZnS carbon composites. The materials were synthesized using wasted pig bristles as sulfur and carbon source and zinc acetate dihydrate as zinc precursor. The materials were synthesized using a one step protocol where pig bristles and zinc acetate dihydrate were heated up in an aqueous diluted solution of KOH. The presence of zinc sulfide phases was demonstrated by XRD and XPS analysis, while the surface area was investigated via SEM, EDX, and N_2 physisorption. The synthesis is a clear example of an easy and sustainable valorization of wasted pig bristles. The protocol can track new paths for substituting sulfur toxic sources with harmless pig bristles.

In addition, the so-produced ZnS carbon materials showed remarkable activity as catalysts for two different oxidation reactions: the oxidation of benzyl alcohol to benzaldehyde and the oxidation of toluene to benzaldehyde. The oxidation of benzyl alcohol plays an important role in the chemical industry, while the oxidation of toluene is extremely captivating as it solves the problem of removing a pollutant through the production of value-added benzyl aldehyde. For both reactions, the most active sample was ZnS-5h, reaching the oxidation of benzyl alcohol up to 63% with 86% selectivity and the oxidation of toluene up to 29% with 87% selectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b04968.

Additional materials characterizations and data of the reuse of the catalysts (PDF)

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Notes

The authors declare no competing financial interest.

Table 3. Conversion and Selectivity Results for the Oxidation of Toluene

	15 min		30 min		45 min	
sample	conversion/%	selectivity/%	conversion/%	selectivity/%	conversion/%	selectivity/%
BLANK	<5	~50	<5	~50	<5	~50
ZnS-1h	7.3	94.1	8.2	89.0	9.2	88.8
ZnS-3h	11.3	88.1	12.1	90.7	12.6	88.1
ZnS-5h	18.8	89.6	28.6	89.8	28.5	86.7

DOI: 10.1021/acssuschemeng.8b04968
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 721290. This publication reflects only the author's view, exempting the Community from any liability. Project website: http://cosmic-etn.eu/. M.J.M.-B. also thanks MINECO for the award of postdoctoral JdC contract (FJCI-2016-29014). The publication has been prepared with support of RUDN University program 5-100.

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