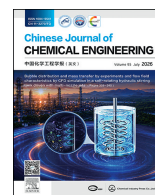




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Full Length Article

Molten salt-derived biochar with tunable pore architecture as non-metallic catalysts for acetylene hydrochlorination

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ABSTRACT

Biochar-based catalysts show significant potential to replace toxic mercuric chloride in acetylene hydrochlorination. However, the mechanistic role of their non-metallic active sites remains scarcely investigated, particularly regarding the synergistic interplay between pore architecture and surface functionalities. Herein, a series of biochar based catalysts with rich microstructures were successfully prepared by using molten salt as medium, which were used in acetylene hydrochlorination. The method of preparing biochar by liquid medium of molten salt was optimized by adjusting the ratio of terpolymer salts, mesh number, constant temperature duration, reaction temperature and heating rate, *etc.* The materials were analyzed by BET, XRD, TGA, SEM and TEM. The results showed that the biochar materials had abundant pore structure and adjustable pore volume, and it was found that biochar with larger pore volume showed higher acetylene hydrochlorination conversion at the same pore size of 1.8 nm. Analysis suggests that biochar with large pore volume has more carbon “chambers” at the micropore size, which effectively promotes the “one-to-one” pairing of C₂H₂ and HCl molecules. This work found that the catalytic performance of acetylene hydrochlorination could be improved effectively by microstructural regulation of nonmetallic catalysts.

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1. Introduction

Vinyl chloride (VCM) is the monomer of polyvinyl chloride (PVC), an engineering plastic widely used in the world. Acetylene hydrochlorination is the main method for producing vinyl chloride [1]. However, the conventional HgCl₂ catalyst, which serves as the primary catalyst for acetylene hydrochlorination, causes significant environmental contamination and human health hazards due to Hg release and bioaccumulation [2,3]. By 2020, China has discussed and explained the mercury content used in the production of PVC [4,5], therefore, the development of environmentally

friendly acetylene hydrochlorination mercury-free catalyst is imminent.

Over the past few decades, researchers have experimented extensively with other metal catalysts to replace HgCl₂ catalysts, including Au [6], Ru [7], Pd [8], Cu [9] based catalysts and so on [10]. Recognized for its superior vinyl chloride selectivity, Au-based catalysts are considered the most promising non-mercury candidates for industrialization [11]. Nevertheless, rapid deactivation from carbon deposition and sintering, alongside their high cost, critically impedes their widespread industrial adoption [12]. Based on the principles of green industrial catalysis for pollution reduction and cost efficiency, carbon-based materials have attracted significant research interest due to their unique properties. Porous carbon materials have been widely applied in catalysis [13]. Some researchers have studied the catalytic performance of acetylene hydrochlorination reaction [14]. Li *et al.* [15] synthesized a porous carbon material using ZIF-8 as a precursor

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and incorporated melamine as an additive to adjust the nitrogen content, which demonstrated certain stability and activity. Qiu *et al.* [16] successfully prepared defect-rich activated carbon through methods such as high-temperature thermal treatment and nitrate-assisted oxidation. Experimental and DFT computational results collectively demonstrate that the catalytic performance for acetylene hydrochlorination is linearly correlated with the surface defect content, confirming these defects as the non-metallic active centers. Ali *et al.* [17] employed DFT calculations to investigate the active sites and reaction mechanisms of nitrogen- and boron-doped carbon materials in acetylene hydrochlorination. It revealed that the pyridinic nitrogen configuration exhibits the highest catalytic activity, and proposed that the balance between C_2H_2 adsorption and HCl activation serves as a key descriptor for enhancing catalytic performance. Biochar (BC) is an abundant carbon material produced by the pyrolysis of biomass under anoxic conditions [18]. BC holds significant potential in heterogeneous catalysis due to its wide availability, low cost, and environmental friendliness [19,20]. However, the application of biochar as a catalyst in acetylene hydrochlorination remains largely underexplored. Therefore, a systematic investigation into the structure-activity relationship of biochar is urgently needed.

Based on the microporous confinement effect [21,22], we discussed the effect of adjustable pore volume in microporous biochar on acetylene hydrochlorination. Try to guess if there are more independent “small rooms” to promote the independent pairing number of C_2H_2 and HCl gas molecules when the pore structure shows a certain range of pore sizes, small pore sizes and large pore volumes, so as to improve the selectivity of acetylene hydrochlorination reaction. The experimental method is different from traditional pyrolysis to produce carbon [23], Molten salt is used as liquid medium [24], Biomass can be transformed into carbon based materials with abundant pore structure through solid liquid phase reaction. Further application in acetylene chlorination reaction.

2. Materials and Methods

2.1. Materials and chemicals

All chemical reagents were used without further processing. The salts for biochar synthesis including K_2SO_4 , KCl and Na_2SO_4 were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The biochar prepared by molten salt was cleaned by HCl to remove impurities, then ultrasonic by acetone and deionized water and dried at 105 °C, HCl (36% to 38%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Acetone (LC grade) was obtained from Fisher Scientific (Fair Lawn, NJ). Ultrapure water was prepared using a Veolia Water Solutions & Technologies (ELGA, PURELAB Chorus). C_2H_2 (gas, purity 99.99%) and HCl (gas, purity 99.99%) were supplied by Minxing Gas Co., Ltd.

2.2. Preparation biochar and its surface modification

The biomass source was waste wood dust. The collected biomass was first washed using ultrapure water several times to remove dirt and then dried in the oven overnight at 105 °C. The dried wood dust was undergoing the following processes of crushing in a powdering machine with a mesh size of 150, soaking in water and drying overnight. The powder was added into the pre-prepared K_2SO_4 -KCl- Na_2SO_4 eutectic salts (Molten salt in varying proportions) with a mixed ratio of 1:2 by mass. The mixed was ground thoroughly and then took reaction in a tubular furnace in N_2 atmosphere for 1 h at 500, 560, 620, 650, 710 °C, respectively (Table S1 and Table S2). The resultant product was re-suspended

into 0.1 mol·L⁻¹ HCl to remove adsorbed metal ions in a water bath at 90 °C for 8 h. After that, the obtained product was washed in DI water until pH near 7 and dried at 80 °C for future use.

Based on the above method, the single factor, like holding time, mesh number, temperature and heating rate, was changed to obtain optimal biochar with rich microporous structure.

2.3. Characterization methods

Field emission scanning electron microscope (FESEM, Nano nova 450) and scanning transmission electron microscopy (STEM, Tecnai G2 F30) were used to monitor the samples' morphology. Selected area electron diffraction (SAED) is used to observe the crystal morphology characteristics of samples through the corresponding relationship between selected morphology observation and electron diffraction structure analysis. Raman spectra for the samples were tested in the scanning range is 100–2200 cm⁻¹ by Raman spectroscopy (Raman, Lap RAM HR 800). The biochar material in terms of surface areas, pore volume and pore size were obtained by the Brunauer-Emmett-Teller (BET) method (BSD – PS 1/2). The products were measured with Cu K α radiation at room temperature with 5 (°)·min⁻¹ over range of 10°–80° in X-ray diffraction (XRD, PANalytical X'Pert PRO). Thermogravimetric differential thermal analysis (TG-DTG, STA409PC) was used to study mass loss at 30–800 °C, a heating rate of 10 °C·min⁻¹, and in an air atmosphere. The functional groups on the surface of biochars were analyzed by Fourier-transform infrared spectroscopy (FTIR, NICOLET IS50 FT-IR) and scanned in the range of 600–4000 cm⁻¹. The C, H, O, N and S in carbon materials were determined by the organic element analyzer (EA-CHNS/O, Elementar UNICUBE).

2.4. Catalysis evaluation

The catalytic performance of acetylene hydrochlorination in a fixed-bed glass reactor was evaluated (i.d. 10 mm). First, the catalyst is weighed into a fixed-bed reactor, and cotton is stuffed in to stabilize the flow. Under the condition of 160 °C, high purity nitrogen (N_2) gas was introduced to purge the reactor for 1 h to remove water, air and other impurities. Then 0.5 h hydrogen chloride (HCl) gas was introduced to activate the catalyst. Next, acetylene (C_2H_2) and HCl gas were mixed at gas space velocity C_2H_2 (GHSV) 50⁻¹ and ratio of C_2H_2 : HCl = 1:1.2. The gas discharged from the reactor is passed into a saturated sodium hydroxide solution (NaOH) to remove unreacted HCl gas, and then the gas chromatography instrument (a Porapak N Packed Column, 6 ft × 1/800 Stainless Steel) is used for analysis. The conversion of acetylene is the main basis for evaluating catalysts activity in acetylene hydrochlorination reaction [10,25]. The specific calculation formula is as follows:

$$\text{Conversion of acetylene} = (1 - \varphi_{AC}) \times 100\% \quad (1)$$

where, φ_{AC} is the volume fraction of acetylene in the product.

3. Results and Discussion

3.1. Primary optimization of pore volume adjustable BC

3.1.1. Biochar synthesis routes

The biomass pyrolysis process is shown in Fig. 1. In the whole process, mixed salt as a medium participates in biomass pyrolysis and recombination. Biomass is composed of cellulose, hemicellulose and lignin [26]. Cellulose and hemicellulose are linear macromolecules made of D-glucanhydride (1–5) as the basic unit and connected by β -(1–4) glycosidic bonds. Under 300 °C, bio-oil (L-

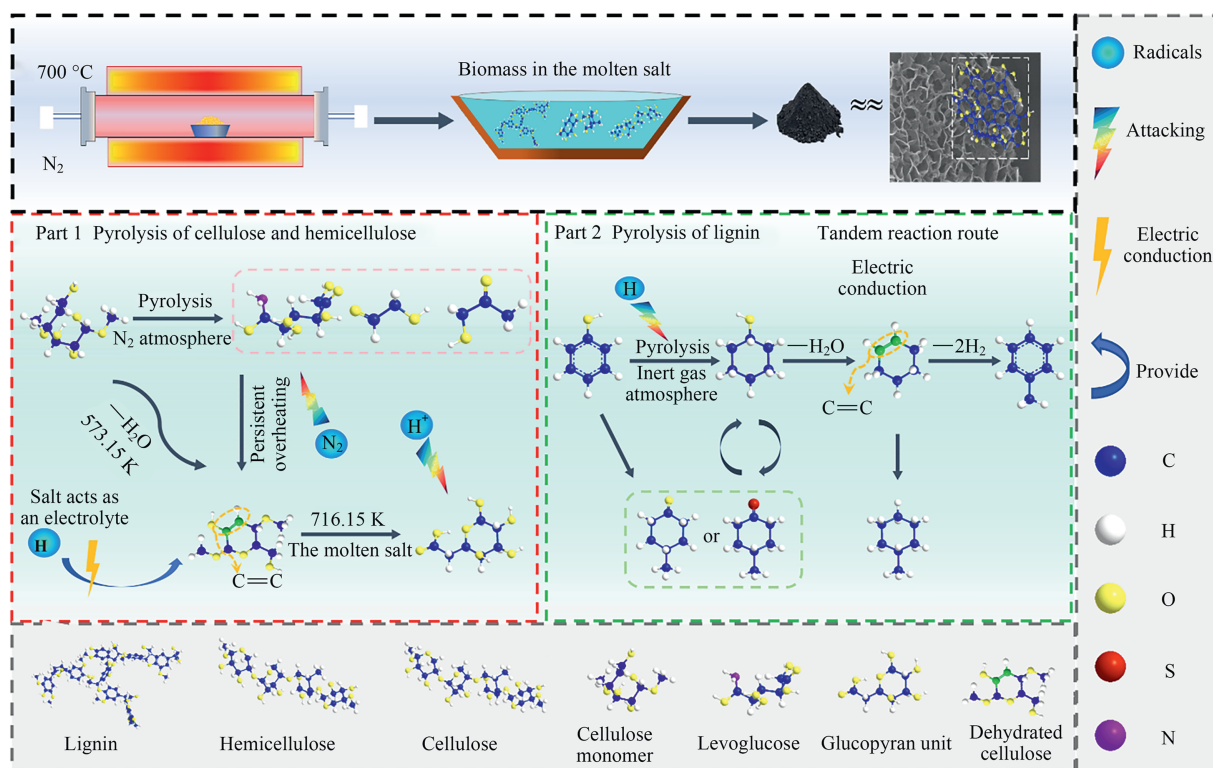


Fig. 1. Route map of biochar synthesis.

glucose), glycolaldehyde and pyruval will be generated, among which L-glucose is easy to volatilize and difficult to maintain for a long time in a high temperature environment. Under N_2 atmosphere, N_2 attacks the molecular structure and appears in the form of NH_2^- . Above 300 °C, cellulose and hemicellulose dehydrate. In general, C—O bond is not easy to break, so —OH is not easy to leave the central carbon atom. The presence of acid can protonate the hydroxyl group, thus forming a good leaving group, H_2O . The dehydration of cellulose is similar to that of alcohols under acidic conditions [27,28]. So the dehydration reaction of cellulose involves an acid catalyst. In the unfused state, the mixed salt can act as an electrolyte to protonate H^+ , accelerate the hydrolysis of glycosidic bonds and promote the reaction. When the temperature rose to 600 °C, the mixed salt began to melt. The introduction of low melting point salt led to the appearance of liquid phase in the synthesis process, which accelerated the diffusion rate of ions and was conducive to the heat transfer efficiency in the carbonization reaction. Biochar rich in special pore structure was produced by virtue of solid-liquid interaction and pyrolysis recombination.

The break of lignin chain forms free radicals, which form decomposition products such as 4-methylphenol by trapping C—H or O—H of other chains which are weaker. With mixed salt as electrolyte to promote protonation and dehydration condensation and other reactions, free radicals react further with other substances, resulting in an increase in chain structure [29]. Finally, the chain reaction terminates when the two free radicals collide with each other to form a stable compound.

3.1.2. Primary optimization of ternary salt

The application of acetylene hydrochlorination in non-metallic catalysts has long been reported [30–33]. However, the selectivity of non-metallic catalysts to acetylene is obviously lower than that of metallic catalysts, so how to improve the selectivity of acetylene

has become a bottleneck for researchers. It is speculated that when acetylene and hydrogen chloride gases are introduced into the catalyst, the selectivity of acetylene will be improved if there are multiple matched room of acetylene and hydrogen chloride. Therefore, constructing a biochar material with microporous structure and adjustable pore volume may be an effective way to improve the selectivity of acetylene hydrochlorination reaction [34]. As shown in Table S1, different ratios of $KCl-K_2SO_4-Na_2SO_4$ was first carried out to become ternary molten salt at theoretical and experimental temperatures [35,36].

The BET of biochar is shown in Table S2, and Fig. 2(a) shows the relationship between temperature and specific surface area and pore volume under the restriction of ternary salt ratio. When $KCl-K_2SO_4-Na_2SO_4=32.5-30.4-37.1$, the optimal specific surface area of biochar is $255.3 \text{ m}^2 \cdot \text{g}^{-1}$ with Ms-BC (620) named, the specific surface area of Ms-BC (500) is relatively poor, $5.8 \text{ m}^2 \cdot \text{g}^{-1}$.

From this, it can be judged that the mixed salt has different internal adjustment ability to the biochar at different temperatures. Below 600 °C, the mixed salt has not been melted, and the biochar can't conduct solid-liquid interaction during pyrolysis and reorganization, and can't effectively control the microstructure of carbon materials. When the temperature reaches 600 °C, it starts to melt, and when the temperature rises to 620 °C, the molten salt fully stimulates the internal pore structure of the biochar. When the temperature continues to rise to 710 °C, the specific surface area suddenly drops to $10.0 \text{ m}^2 \cdot \text{g}^{-1}$, guess that it may be caused by biomass transfer, chemical corrosion and other phenomena in the molten salt system.

3.1.3. Primary optimization of mesh number and constant temperature time

Some researchers [36,37] put forward that the pore structure and specific surface area can be effectively improved by changing

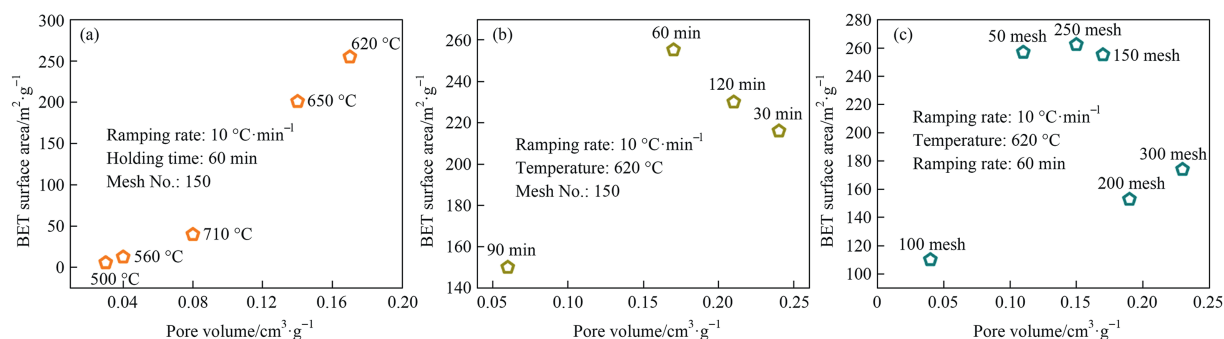


Fig. 2. The relationship between pore volume and specific surface area of the preparation conditions of BC with (a) different molten state of mixed salt in temperature, (b) different constant temperature time, and (c) different mesh numbers.

the mesh number and constant temperature time of carbon materials, they conducted a single factor test on the density change of the determined fiber mesh range (40–100 mesh (0.15–0.42 mm), 20–120 mesh (0.12–0.85 mm), 10–130 mesh (0.11–2.05 mm)) to change the density of specimens in different fiber mesh ranges and explore the influence of density change on the mechanical properties of specimens. 40–100 mesh fiber shape is better, and the density is set as $0.65 \text{ g} \cdot \text{cm}^{-3}$; 20–120 mesh fiber morphology takes the second place, and the density is set as $0.70 \text{ g} \cdot \text{cm}^{-3}$; 10–130 mesh fiber has poor morphology, the density is set as $0.75 \text{ g} \cdot \text{cm}^{-3}$, and it is believed that the mechanical properties can be improved by changing the density under the condition of poor fiber morphology.

The residence time significantly influences the specific surface area and morphology of carbon materials. So Ms-BC (620) will be used for the next step of the mesh number and constant temperature time exploration. The BET of biochar changing the constant temperature time are shown in Table S2. In a certain range, the influence of constant temperature time on the specific surface area and pore structure of biochar is obvious as shown in Fig. 2(b). When the constant temperature time of carbon materials is 60 min, the specific surface area is $255.3 \text{ m}^2 \cdot \text{g}^{-1}$, the pore volume is $0.17 \text{ cm}^3 \cdot \text{g}^{-1}$, and the pore diameter is 1.8 nm, choosing 60 min can obtain large specific surface area and pore volume with relatively less energy consumption, the BET of biochar changing the mesh number are shown in Table S2. The specific surface area of biochar fluctuates to some extent due to the regulation of biomass mesh number as shown in Fig. 2(c). Under the concern of micropore

structure, the specific surface area of biochar can be maintained when the mesh number is 150 and the pore volume is larger.

3.2. Precisely adjustment of BC micropore volume

The BET micropore structure data of biochar changed with temperature, as shown in Table S2 and Fig. 3(a).

When calcination temperature was adjusted in the molten state of tere-salt, the specific surface area of biochar prepared at 700 °C increased to $712 \text{ m}^2 \cdot \text{g}^{-1}$ under the condition of maintaining the micropore structure. Pore volume up to $0.32 \text{ cm}^3 \cdot \text{g}^{-1}$. The pore size distribution also changed significantly. However, when the temperature rises further, there is a significant drop and it is not even possible to harvest biochar material. It was judged that high temperature would lead to the gasification of biochar in the molten salt system. For the nature of the chemical reaction between carbon and carbon dioxide, simply speaking, CO_2 molecules in the gas phase are adsorbed by carbon surface atoms, and then the CO_2 molecular bonds are stretched, twisted, weakened and even broken with the increase of temperature, forming two groups on the carbon surface, ketone group ($\text{C}=\text{O}$) and vinyl acetone ($\text{C}=\text{C}=\text{O}$), of which vinyl acetone has poor stability, and begins to decompose at 600–700 °C, releasing carbon monoxide. Only the ketone group is relatively stable and hardly decomposes below 900 °C.

Purichaya Kuptajit *et al.* [38] investigated the effect of heating rate on pore formation in activated carbon. Comparing KOH-activated carbon prepared via microwave heating with that from conventional conduction heating revealed significant variations in surface area due to heating rate. Combining this with molten salt

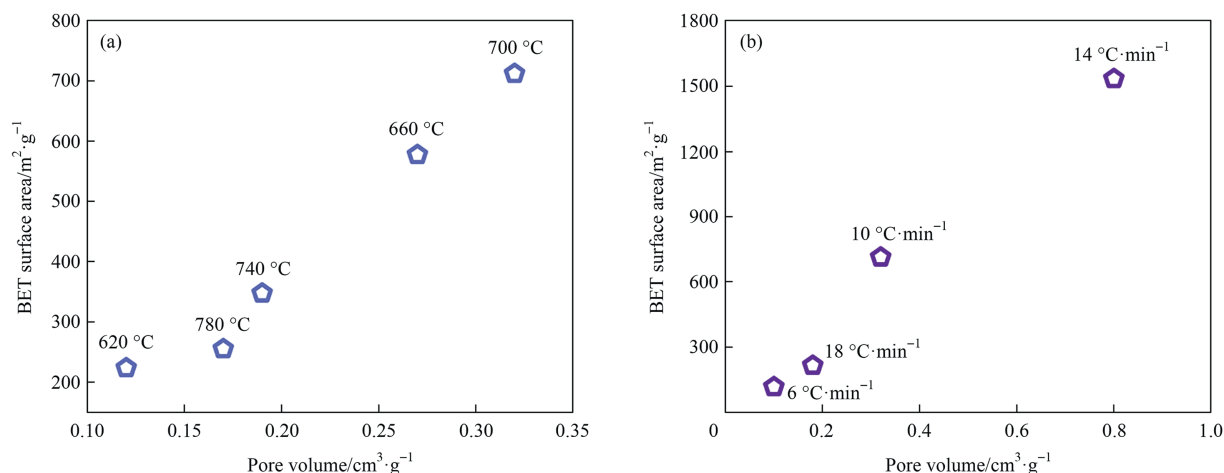


Fig. 3. The relationship between pore volume and specific surface area of the preparation conditions of BC with (a) different temperatures of mixed salt in molten state, and (b) different heating rates.

pyrolysis, precise control of heating rate can effectively regulate the microporous structure of biochar. This is because biomass components (cellulose, hemicellulose, lignin) undergo reorganization during cracking in the mixed molten salt, which involves solid-liquid phase reactions. Different heating rates alter the fluid state of the molten salt: a slow rate leads to slower biomass cracking, promoting levoglucosan and tar formation, thereby reducing biochar yield; an excessively high rate accelerates pyrolysis but increases turbulence in the molten salt, hindering orderly rearrangement of cracked carbon and resulting in biochar with suboptimal micropore volume and specific surface area. We will regulate different heating rates of $6\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (S-BC), $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (T-BC), $14\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (F-BC), and $18\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (E-BC). As shown in Table 1, the pore volume could be changed while the pore size remained relatively unchanged. When the heating rate was $14\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, the specific surface area was up to $1533.0\text{ m}^2\cdot\text{g}^{-1}$, and the pore volume was up to $0.8\text{ cm}^3\cdot\text{g}^{-1}$. And the micropore volume is up to $0.70\text{ cm}^3\cdot\text{g}^{-1}$.

The relationship between pore volume and specific surface area of BC at different heating rates. As show in Fig. 3(b), we can clearly see that the pore volume and specific surface area of BC prepared at $14\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ show obvious advantages. To verify our hypothesis

that modulating the heating rate can optimize the microporous structure of carbon materials and thereby enhance their catalytic activity in acetylene hydrochlorination, a comprehensive characterization study was conducted on the sample prepared under optimal conditions (F-BC, heating rate: $14\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$).

3.3. Characteristics and properties of F-BC

As shown in Fig. 4(a) and (b), it can be seen from the adsorption-desorption curve that F-BC presents a I-type isotherm, which bends to P/P_0 , and the subsequent curve is horizontal or nearly horizontal. The adsorption capacity increases rapidly under low pressure and reaches saturation under certain pressure, similar to Langmuir adsorption isotherm, with micropores playing a dominant role. For nitrogen adsorption, the pore size distribution range of micropores is relatively wide, and they may also have narrow mesopores. The general pore width of such materials is less than 2.5 nm . In addition, I-type isotherm is indicative of micropore filling in adsorbents like carbon materials [39]. From the pore size distribution map (Fig. S2), it can be found that a large number of pore sizes are distributed at $<2\text{ nm}$. Combined with the curve

Table 1
Effect of heating rate on pore structure in molten state.

Ramping rate/ $^{\circ}\text{C}\cdot\text{min}^{-1}$	BET surface area/ $\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{micro}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{micro}}/\text{cm}^3\cdot\text{g}^{-1}$	Pore volume/ $\text{cm}^3\cdot\text{g}^{-1}$	Pore size/nm
6	116.0	104.9	0.05	0.10	1.7
10	712.2	643.4	0.32	0.42	1.8
14	1533.0	1442.9	0.70	0.80	1.8
18	214.5	182.1	0.10	0.18	1.8

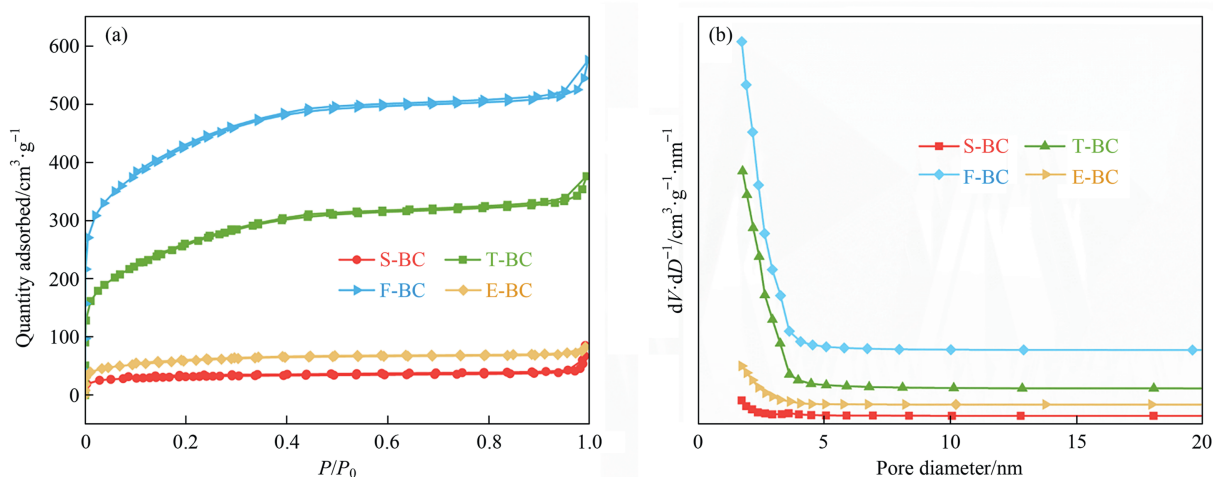


Fig. 4. (a) N_2 adsorption isotherms and (b) pore size distribution of different biochar samples.

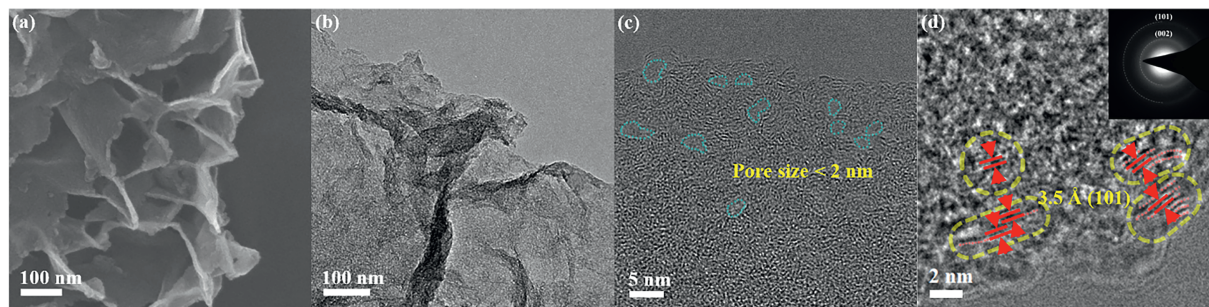


Fig. 5. (a) SEM, (b) TEM, (c) SAED and HRTEM of F-BC.

trend and pore sizes in Table 1, we can conclude that the pore sizes are mainly concentrated around 1.8 nm.

The morphology and structure of F-BC were characterized by SEM, TEM, SAED and HRTEM (Fig. 5).

As shows in Fig. 5(a), a unique macroporous structure (pore diameter >50 nm) with ultra-thin nano sheets. From the visual effect, the structure is similar to a honeycomb. The micropore has an effective radius (<2 nm) of the same order as the molecule of the adsorbed material, which is the most important pore structure of carbon materials and determines the size of adsorption amount. The inner surface of microporous carbon is essentially different from that of non-porous carbon due to the relative avoidance of overlapping of adsorption force field, which affects the adsorption mechanism. Macropores (>50 nm) and mesopores (2–50 nm) provide the adsorption mechanism of the surface. To investigate the rich microporous structure of the biochar, we employed TEM and HRTEM. It can be observed that there are dense and evenly distributed white dots (Fig. 5(b) and (c)), which are microporous. We compared the pore size distribution of the F-BC (Fig. S2), and it can be seen that the proportion of the pore size between 1.7 nm and 1.9 nm is the highest, about 35.5%, until the micropores are dominant. The HRTEM image (Fig. 5(d)) of the biochar material above shows that the lattice stripes with a width of about 0.35 nm correspond to the (0 0 2) crystal plane of carbon, which is consistent with the results of XRD (Fig. 6(a)), the selected electron diffraction (SAED) diagram of the biochar material also shows that the biochar material has crystal planes, which shows that the

prepared samples tend to be graphitized. Through the analysis of the morphology and structure of the prepared samples, it is shown that F-BC are inclined to be graphitized a biochar material with abundant micropores and resembles a honeycomb pattern.

The XRD spectra of F-BC are shown in Fig. 6(a), the bulk phase structure information of the material can be obtained by X-ray. The amorphous diffraction peaks of F-BC at 25° and 43° correspond to the crystal plane (0 0 2) and (1 0 1) of carbon respectively, which are consistent with the crystal plane of graphite. No characteristic peaks of other impurities are found. This phenomenon corresponds well with the observation in the TEM image, it was indirectly verified that the synthesized carbon materials tended to be graphitized [40]. To identify the effects of F-BC on pyrolysis process, the thermogravimetric (TG) and derivative thermogravimetric (DTG) experiments of BC was conducted (Fig. 6(b)). Mass loss of BC was found between 400 °C and 560 °C, resulting in about 94%, of which TG mainly had two mass loss stages, the water separation stage (room temperature to about 132 °C) and the volatilization precipitation stage (>132 °C), because the thermal stability of lignin is higher than that of hemicellulose and cellulose, in the volatilization and precipitation stage, half cellulose begins to decompose at 220–315 °C, while cellulose decomposes in the temperature range of 315–400 °C [41]. As the temperature rises to 400 °C, mainly lignin is decomposed. When the temperature is higher than 400 °C, the TG curve has the characteristics of accelerated mass loss [42]. When the temperature is higher than 560 °C, the mass does not continue to

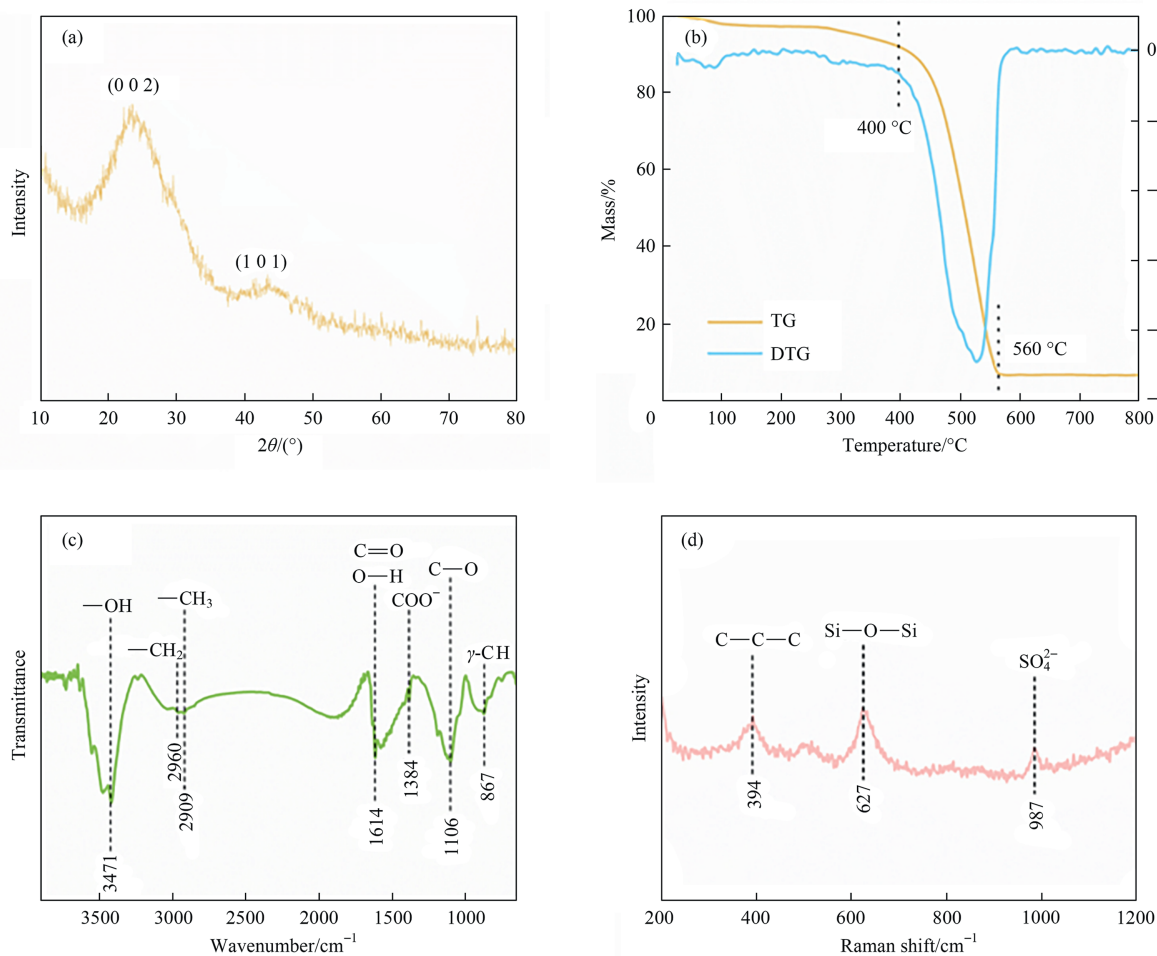


Fig. 6. (a) XRD patterns, (b) TG and DTG curves, (c) FT-IR transmittance spectra, and (d) Raman spectrum (200–1200 cm⁻¹) of F-BC.

decrease with the increase of temperature, indicating that the sample BC undergoes complete oxidative decomposition. At the end of the mass loss, there is still 4% of the mass residue. Combined with the elemental analysis of (Table S3), EDS elemental mapping analysis of (Fig. S3), it is judged that there is still a small amount of salt residue.

The demonstrative evidence in FTIR analysis is shown in Fig. 6(c). The absorption band with a peak at 3471 cm^{-1} is caused by the stretching vibration of the —OH group [43], indicating that there are some hydroxyl groups on the surface of the biochar sample. The bands around 2960 cm^{-1} and 2909 cm^{-1} belong to the long-chain aliphatic components —CH_2 and —CH_3 groups, respectively [44]. The characteristic peaks around 1614 cm^{-1} are mainly related to the C=O stretching vibration of the ester and the O—H stretching vibration [45]. The peak near 1384 cm^{-1} is related to the COO^- group, 1106 cm^{-1} belongs to the C—O bending vibration [46]. The weak band at about 867 cm^{-1} was due to the $\gamma\text{—CH}$ of furans [47]. According to the analysis results of organic elements (Table 2), the high O/C and (O + N)/C ratios of F-BC relative to its H/C ratio point to the surface of biochar was rich in functional groups, including aromatic rings, COO^- , —OH , and C=O . These elemental data corroborate the FTIR findings; together, they confirm that the biochar possesses a surface chemistry conducive to strong physicochemical adsorption [48].

The Raman spectrum of the $200\text{—}1200\text{ cm}^{-1}$ band is shown in Fig. 6(d). The peak near 394 cm^{-1} is related to the C—C—C shear deformation [49], and the 987 cm^{-1} is the SO_4^{2-} characteristic peak in K_2SO_4 and Na_2SO_4 [50]. Organic element analysis and EDS analysis of elements (Fig. S3 and Table S3) combined with Table 2 shows that a small amount of molten salt remains in the sample. At the same time, it was found that a fixed spectral peak appeared at $600\text{—}800\text{ cm}^{-1}$, which was found to be the Si—O—Si symmetric stretching vibration peak, which was caused by the direct detection of Raman spectrum in the glass balancer.

In order to more accurately describe the structural characteristics of F-BC, the Raman spectrum in the range of $800\text{—}2000\text{ cm}^{-1}$ were subjected to peak fitting (Fig. 7). There are two peaks which represent the D-band peak and the G-band peak. The D band is the defect activation band in SP^2 hybrid carbon, corresponding to the bond in the carbon material lattice due to hybrid atom doping or plasma etching. Angular disorder, small bond disorder, and defects due to hybridization. G-bands are caused by in-plane vibrations of carbon atoms and represent ordered carbon [51,52]. The D_1 peak located near 1350 cm^{-1} corresponds to the C—C vibration between aromatic sheets, which is related to the lattice imbalance at the edge of the graphite microplatelets or the in-plane defects caused by heteroatoms [53]. The vibration type of the D_2 peak near 1590 cm^{-1} is the same as the G peak, which is E_{2g} , but the D_2 peak is affected by the stretching vibration of the C—C bond between the graphite layers, and the intensity decreases with the increase of the order degree of the carbon material. The D_3 peak near 1540 cm^{-1} appears as a broad peak, which is generated by amorphous carbon in SP^2 mode, such as organic molecules, fragments or functional groups in carbon materials with a high degree of disorder, which are usually reacted by carbon materials. active point [54]. The D_4 peak near 1240 cm^{-1} is strengthened with the

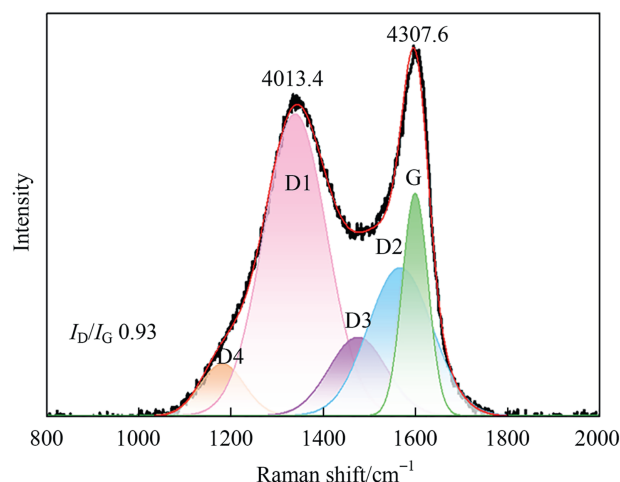


Fig. 7. Curve-fitting Raman spectrum ($800\text{—}2000\text{ cm}^{-1}$) of F-BC.

increase of disorder, which may be attributed to the C—C vibration between aromatic rings and alkanes, the C—C vibration between aromatic rings and ethers, and the C—C vibration between hydrogenated aromatics. In addition, the ratio of D-band to G-band (I_D/I_G) is often used to describe the degree of defects in carbon materials [48].

3.4. Evaluation of catalyst

The catalytic performance of biochar samples (constant pore size: $\sim 1.8\text{ nm}$; varied pore volume via heating rate) was evaluated in acetylene hydrochlorination at $160\text{ }^\circ\text{C}$, space velocity 50 h^{-1} , atmospheric pressure and raw gas $V(\text{HCl})/V(\text{C}_2\text{H}_2) = 1.2$. The biochar prepared at $14\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ (F-BC, pore volume of $0.80\text{ cm}^3\cdot\text{g}^{-1}$, pore size of 1.8 nm) showed the highest catalytic performance among all tested samples (Fig. 8), and the conversion of acetylene achieved 26% that surpasses most reported counterparts even at a lower temperature (Table S4). In the 12 h catalyst evaluation stage, although the conversion rate of acetylene (C_2H_2) was not high, the conversion curve showed no obvious downward trend, indicating that biochar as a carbon-based catalyst has high stability and is not easy to be inactivated, thus proving that biochar materials have

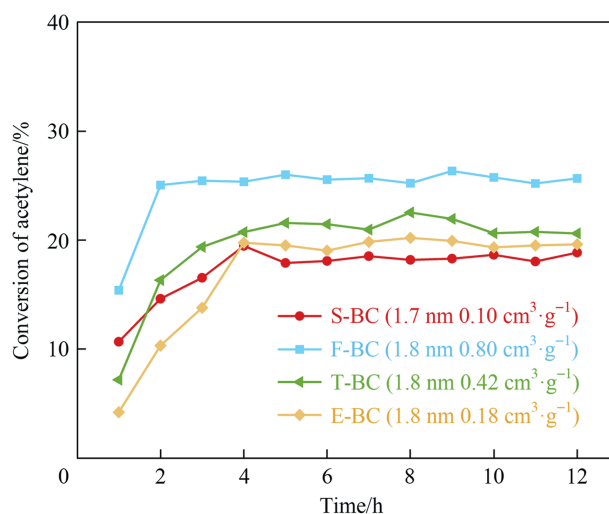


Fig. 8. Acetylene conversion over different biochar samples. $T = 160\text{ }^\circ\text{C}$, $\text{GHSV}(\text{C}_2\text{H}_2) = 50\text{ h}^{-1}$, $V(\text{HCl})/V(\text{C}_2\text{H}_2) = 1.2$.

Table 2
Analysis of organic elements in F-BC.

Material	Organic element analysis					Atomic ratio		
	C/%	N/%	H/%	O/%	S/%	H/C	O/C	(O + N)/C
F-BC	50.16	1.39	1.56	22.90	6.07	0.03	0.46	0.48

infinite potential as carbon-based catalyst for acetylene hydrochlorination.

To further explore the relationship between pore structure and catalytic performance, the BET-derived pore size and volume were included in the analysis (Fig. 8). The pore size of each biochar was about 1.8 nm, and the acetylene conversion rate increased with the increase of pore volume. Therefore, it is concluded that biochar with microporous structure with the increase of pore volume means that numerous independent “small chamber” structures are generated inside, and these small chambers can improve the pairing rate of HCl and C₂H₂ gas molecules, so as to improve the conversion rate of acetylene hydrochlorination.

4. Conclusions

By introducing eutectic molten salt liquid phase medium, a new type of biochar material rich in microscale pore volume was prepared successfully. Systematic optimization of molten salt composition, biomass mesh number, reaction temperature, constant temperature duration, and heating rate enabled precise pore size control at 1.8 nm, with microscale pore volume of biochar effectively regulated from 0.1 to 0.8 cm³·g⁻¹. The specific surface area, surface properties, elemental composition and microstructure (such as pore size, pore volume and carbon atomic structure defects) of the carbon-based catalyst have been systematically tested and analyzed by XRD, BET, Raman, TEM, HRTEM, SEM, FT-IR and TGA characterization methods. The catalytic performance of biochar was evaluated by the acetylene hydrochlorination. Setting the reaction temperature at 160 °C, space velocity at 50 h⁻¹ and the ratio of raw gas V(HCl)/V(C₂H₂) = 1.2, it was found that F-BC with pore volume of 0.8 cm³·g⁻¹ exhibited higher conversion of acetylene (≥26%) than other biochar samples with smaller pore volumes at the same pore size. It can be concluded that biochar with larger pore volume value at 1.8 nm pore size has more independent “chambers”, which can improve the single pairing rate of C₂H₂ and HCl gas molecules, which is the key to improve the catalytic performance of carbon-based acetylene hydrochlorination.

CRedit Authorship Contribution Statement

Jun-Long Li: Writing – review & editing, Writing – original draft, Project administration. Dong-Yang Zhao: Writing – review & editing, Writing – original draft, Project administration. Jia-Yi Dong: Data curation. Mian Hu: Methodology, Formal analysis. Jia Zhao: Methodology, Data curation. Zhiyan Pan: Resources, Formal analysis. Jun Zhao: Writing – review & editing, Validation, Conceptualization. Xiaonian Li: Resources, Conceptualization. Zhong-Ting Hu: Writing – review & editing, Validation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

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