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Research article

## New perspectives on the effects of texture and chemical properties on the hydrogen storage capacity of biochar at room temperature



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ARTICLE INFO	A B S T R A C T
Keywords: Biochar Pore structure Oxygen-containing groups KOH activation Hydrogen storage	Analyzing the effects of texture and chemical structure on hydrogen adsorption performance at room temper- ature can provide a theoretical basis for accurately constructing carbon-based hydrogen adsorbents. Based on thermal regulation technology, the biochar with different specific surface areas ( $803.85-2801.88 \text{ m}^2/\text{g}$ ) and oxygen content ( $21.57-41.86\%$ ) was successfully prepared by the two-step "carbonization-activation" method. Various characterization methods were used to explore the relationship between the physicochemical structure and hydrogen adsorption characteristics at room temperature. The results show that the hydrogen storage characteristics of biochar at room temperature are controlled by specific surface area, oxygen content, and acidic surface groups. The boundary conditions for promoting/inhibiting hydrogen adsorption are related to oxygen content. In different pressure regions, specific surface area, oxygen content, and the acid surface group have different degrees of effect on hydrogen adsorption, and oxygen content has the most significant impact. The Freundlich model accurately fits the hydrogen adsorption process at room temperature. Among the carbon-based hydrogen storage materials, biochar has excellent hydrogen storage performance, with an adsorption capacity of 0.52 wt% at 50 bar.

#### 1. Introduction

Hydrogen plays a vital role in solving global warming issues and achieving carbon neutrality goals due to its high energy density and zero-carbon properties. However, hydrogen's low bulk density (low energy density per unit volume) makes storage or transportation extremely difficult and expensive. Therefore, it is significant to develop advanced hydrogen storage technologies to accelerate the use of hydrogen as an energy carrier [1]. Compared with high-pressure gaseous compression and cryogenic liquid hydrogen storage, solid hydrogen storage has more advantages in cost and safety [2,3]. Among the solid-state hydrogen storage materials, carbon-based materials have good development prospects owing to the benefits of low skeleton density, fast adsorption/desorption rate, high chemical and thermal stability, and accessible design and processing [4,5].

Hydrogen is stored in solid materials through physical adsorption, chemical adsorption, or chemical reaction. Carbon-based materials are mainly based on van der Waals forces for physical adsorption to capture hydrogen. At low temperatures, activated carbon with a high surface area shows excellent hydrogen storage capacity compared to other carbon-based materials, such as carbon nanotubes and nanofibers [6–8]. However, all carbon-based materials have a low hydrogen storage capacity at room temperature [7,8]. Designing and developing carbon-based materials with high hydrogen storage capacity at room temperature and low pressure is attractive and challenging.

Some existing theoretical studies have shown that activated carbon has a low coverage of hydrogen adsorption at room temperature, so the influence of surface groups may be significant [9–12]. Agarwal et al. [ [13]] found that the hydrogen storage capacity of activated carbon increases with the number of oxygen-containing groups. Carbon oxidation can produce more attractive surfaces at low pressures and coverage [14,15]. More defect sites and active adsorptive sites can be produced by the addition of oxygen-containing groups, improving the interaction between the surface of carbon-based materials and adsorbents and encouraging hydrogen adsorption on the carbon surface [16,17]. Baytar et al. [18] showed that various oxygen-containing groups, such as alcohols, phenolic hydroxyl groups, carbonyl groups, and carboxyl groups, can enhance the adsorption capacity of carbon-based materials.

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#### Table 1

Proximate and ultimate analysis of corn straws.

Sample	Proximate analysis(wt%)			Ultimate an	Ultimate analysis(wt%)				
	Mad	A <sub>ad</sub>	V <sub>ad</sub>	FCad	C <sub>ad</sub>	H <sub>ad</sub>	O <sub>ad,*</sub>	Nad	S <sub>ad</sub>
Corn straws	9.40	1.30	71.00	18.30	43.28	5.60	50.39	0.63	0.10

Note: ad = air dry basis, \* = by difference.

Han et al. [19] found that the order of oxygen-containing groups to enhance the hydrogen storage capacity is as follows: cis-COOH functionalized  $\geq$  trans-COOH>OH. However, Huang et al. [20] and Lee et al. [21] found that the hydrogen storage capacity of carbon-based materials decreases after acid oxidation. And the oxygen-containing groups can inhibit hydrogen adsorption on activated carbon through steric hindrance in pores and increased adsorbent mass [22,23]. In conclusion, there needs to be a consistent analysis of how oxygen-containing structure affects hydrogen adsorption in carbon-based materials. Clarifying the impact of oxygen-containing groups' type and quantity on carbon-based materials' hydrogen storage properties is crucial, especially at room temperature. So, this study examines how oxygencontaining structures affect hydrogen adsorption for biochar with a porous structure.

KOH activation can enhance the adsorption capacity of carbon-based materials by developing pore structures and manufacturing defect sites. Thus, KOH is widely used in the preparation process of carbon-based hydrogen storage materials. Since the reactivity of oxygen-containing groups is higher than that of carbon-containing groups, the chemical reaction between oxygen-containing groups and KOH may be more potent than that between carbon-containing groups and KOH. Therefore, various surface functional groups (such as carboxyl, phenolic, hydroxyl, and carbonyl) are introduced to change the chemistry of carbonbased materials during KOH treatment [24]. Chen et al. [25] found that KOH can form active vacancies by reacting with biomass, and OH- from KOH can quickly occupy these vacancies to introduce oxygen, creating a large number of new O-containing groups in biochar, and the O-containing groups further transform into more stable -OH, C-O and -COOH groups with an increase in reaction temperature. Hu et al. [26] found that under the low KOH/Char ratio, KOH can increase the formation of oxygen-containing groups during the thermal conversion in an inert atmosphere. However, the quantitative description of the effect of KOH activation on the construction of oxygen-containing structure and its correlation with hydrogen storage capacity needs to be further studied.

In this work, we prepared a series of biochar-based hydrogen storage materials under different activation temperatures and KOH/Char ratios. The samples before and after activation were pickled to prevent the potential impact of alkalis and alkaline earth metals(AAEMs) on the hydrogen adsorption capacity. Various analytical methods such as N<sub>2</sub> adsorption, scanning electron microscopy(SEM), X-ray diffraction (XRD), elemental analysis(EA), X-ray photoelectron spectroscopy(XPS), and temperature programmed desorption(TPD) were used to quantitatively analyze the changes in morphology and oxygen-containing groups after activation. The influence of biochar's pore structure and chemical properties on hydrogen storage at room temperature is explored in depth, which provides a theoretical basis for understanding the impact of oxygen-containing groups on hydrogen storage characteristics of carbon materials and the subsequent modification of surface oxygencontaining groups to strengthen hydrogen storage capacity.

#### 2. Experimental and methods

#### 2.1. Materials

Table 1 shows the ultimate and proximate analysis of the corn straw which was produced in the surrounding areas of Harbin in China. The corn straw shows prominent "oxygen-rich and low-carbon" characteristics and the oxygen content is as high as 50.39%.

#### 2.2. Biochar preparation, pickling, and activation

Fig. 1 shows the preparation process of biochar, which is divided into steps such as crushing and sieving, pickling, carbonization, and activation. The working conditions of carbonization and KOH activation are shown in Table 2. The heating rates of carbonization and activation are 10 °C/min and 5 °C/min, respectively. And it is maintained for 30 min after reaching the target temperature. More details on the experimental operation can be found in our previous work [27].



Fig. 1. Two-step "carbonization-activation" experimental process.

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Table 2

Preparation processes of biochar samples.

Sample	Treatment process	Atmosphere	KOH/char(Mass ratio)	Sample mass (g)
Biomass	Carbonization at 600 °C	N <sub>2</sub> /1L/min	-	4
H-biochar	Activation at 700 °C	N <sub>2</sub> /1L/min	1:1	2
H-biochar	Activation at 800 °C	N <sub>2</sub> /1L/min	1:1	2
H-biochar	Activation at 900 °C	N <sub>2</sub> /1L/min	1:1, 2:1, 3:1, 4:1	2
H-biochar	Activation at 1000 °C	N <sub>2</sub> /1L/min	1:1	2

0.2 mol/L of  $H_2SO_4$  (40:1 according to liquid-solid mass ratio) is used for pickling biochar to prevent the effect of AAEMs on the activation process and hydrogen adsorption. After each pickling, repeat washing with deionized water until the pH of the washing solution is constant, as detailed in the literature [28,29]. The biochar carbonized at 600 °C is named H-biochar after pickling. The activated biochar is named CS-A-B. CS represents straw, A represents activation temperature, and B represents activation ratio. For example, CS-900-1 is the biochar obtained by H-biochar at an activation temperature of 900 °C and a KOH/biochar mass ratio of 1:1.

#### 2.3. Material characterization

The pore characteristics of biochar were analyzed using BSD-PM high-performance specific surface area analyzer (Beijing Beishide Company). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore volume and pore size were determined by the Barrett-Joyner-Halenda (BJH) method and the Horvath-Kawazoe (H—K) method.

Scanning electron microscopy (SEM, Regulus8100) was used to observe the apparent morphology of biochar. The accelerating voltage is 0.5-30 kV, and the secondary electron resolution is 0.8 nm (accelerating voltage 15 kV). 50,000 magnifications characterize some areas with typical morphological structures.

The microcrystalline structure of biochar was quantitatively characterized by an X-ray diffractometer (Rigaku SmartLab). The accelerating voltage and current intensity were 40 kV/30 mA, the X-ray wavelength was 0.154056 nm, the scanning range was  $2\theta = 5-80^{\circ}$ , and the scanning interval and scanning rate were  $0.01^{\circ}$  and  $10^{\circ}$ /min, respectively.

An organic element analyzer (German Vario Micro Cube) was used to analyze the change of biochar C/H/O element content before and after activation. Using C/H/N/S mode testing, O content is obtained using the difference subtraction method.

XPS testing was performed using an X-ray photoelectron spectrometer (Thermo Fischer, USA, ESCALAB 250Xi). The excitation source adopts Al ka ray (hv = 1486.6 eV), the working voltage is 12.5 kV, the filament current is 16 mA, and the signal accumulation is carried out about 10 cycles. Passing-Energy is 30ev in steps of 0.1 eV.

#### 2.4. TPD test

Biochar is fully dehydrated in advance for 12 h in a drying oven at 105 °C, and the sample mass for each experiment was  $20 \pm 0.05$  mg. The TPD procedure is as follows: heated from room temperature to 110 °C under an N<sub>2</sub> atmosphere, held for 10 min, and then heated to 1000 °C. The heating rate is 5 °C/min, and the N<sub>2</sub> flow rate is 0.5 L/min. The composition of experimental exhaust gases was monitored online using the MCA 100 SYN type synthesis gas analyzer from ETG RIORSE E TECNOLOGIA in Italy, focusing on CO and CO<sub>2</sub> yield, with an accuracy of ±2%. The following formulas(1–3) calculate gas production.

$$Q_x = \frac{V_{N_2} \times Gasratio_x}{60 \times Gasratio_{N_2}}$$
(1)



Fig. 2. Scanning electron microscopy and pore analysis results of biochar samples (a) Reaction mechanism diagram of KOH (b) Development of specific surface area (c) Scanning electron microscopy photo of CS-900-4(d)Development of pore volume.

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Fig. 3. Model of XRD pattern and carbon layer stacking (a) XRD spectra of biochar samples; (b) Schematic diagram of the change of the carbon sheet layer after activation.

$$n_x = \frac{Q_x \times 10^9}{m \times 22.4}$$
(2)

$$n_{cf} = \int_0^t n_x dt \tag{3}$$

 $Q_x$  stands for the volumetric flow rate per unit time of generated gas, L/s; x stands for CO or CO<sub>2</sub>; V<sub>N2</sub> stands for N<sub>2</sub> traffic, L/min; Gas<sub>ratiox</sub> represents the instantaneous concentration of CO/CO<sub>2</sub>, and Gas<sub>ratioN2</sub> represents the instantaneous concentration of nitrogen, %; n<sub>x</sub> represents the amount of biochar CO or CO<sub>2</sub> generated per second, µmol/g/s; m represents sample mass, g; n<sub>cf</sub> represents the total active bit quantity of biochar per unit mass, µmol/g; t stands for reaction time, s.

#### 2.5. Hydrogen uptake measurements

Biochar is first degassed in a vacuum at 300 °C for 120 min. Hydrogen adsorption isotherms with a room temperature of 25 °C and a 1–50 bar pressure range were collected using a PSD-PH device. The pressure accuracy of the device reaches 0.01%FS, and the temperature control accuracy is  $\pm 0.1$  °C. The experimental data were described using Freundlich and Langmuir adsorption models to understand the relevant factors affecting hydrogen adsorption capacity. The model formula and more details can be consulted [27].

#### 3. Results and discussions

#### 3.1. Surface morphology and pore characteristics

The KOH activation mechanism and the test results for  $N_2$  adsorption and SEM are summarized in Fig. 2. The specific activation mechanism is shown in Fig. 2-a. In the "carbonization-activation" step, biochar pores undergo processes such as "generation-expansion-merger" and gradually develop into pores dominated by micropores. With the gradual increase of activation temperature, the dissolution of SiO<sub>2</sub> in char, the further activation of  $CO_2$  decomposition from  $K_2CO_3$ , and the expansion of the carbon lattice by interpolating metal K in the carbon sheet layer all promote the development of pores [30]. A higher proportion of KOH/ char can produce a sizeable gaseous metal K, promoting K intercalation penetration. During the activation process, the active components such as  $K_2O$ ,  $K_2CO_3$ , and gaseous metal K are affected by the activation ratio and temperature, which can affect porosity differently.

Fig. 2-b shows that biochar's BET and microporous specific surface areas are growing steadily with the increased activation temperature. When the temperature increased from 700 °C to 1000 °C, the BET area and the microporous specific surface area increased by 1.44 times. As the temperature rises to 900 °C and the activation ratio increases to 4:1, the pores have developed extensively. Moreover, the BET and microporous specific surface areas have a significant trend, increasing by 2.51 times. Fig. 2-d shows that the increase in the activation ratio can encourage the development of pores below 0.7 nm and 2 nm. The CS-900-4 with the largest specific surface area was selected for further surface morpholopy analysis, as shown in Fig. 2-c. The biochar surface with fully developed pores is distributed with fine micropores. The outer surface is still relatively smooth, reflecting the gradual transfer of the KOH activation process from the inside of the biochar to the outside.

#### 3.2. Development of microcrystalline structures

XRD test was used to analyze the change law of the biochar carbon sheet layer after activation. According to the results, the microcrystalline structure data of biochar was further calculated, and the processed XRD test data were shown in Fig. 3-a. The XRD spectra of all samples showed two diffraction peaks at  $2\theta = -23^{\circ}$  and  $-43^{\circ}$ , peak 002 with aromatic stack size and peak 100 with aromatic sheet size. The angle corresponding to the diffraction peak increases slightly with the increased activation temperature and ratio.

According to the Bragg formula and the Scherrer formula [31] such as (4), (5), (6), combined with the peak position and half-width of 002 and 100 peaks, the layer spacing d002, microcrystalline width  $L_a$ , and

Table 3

Graphite microcrystalline structure data of biochar samples.

	d <sub>002</sub> (nm)	L <sub>a</sub> (nm)	L <sub>c</sub> (nm)	Ν
CS-700-1	0.360	3.095	0.769	2.14
CS-800-1	0.361	3.201	0.727	2.02
CS-900-1	0.360	3.423	0.770	2.14
CS-1000-1	0.356	3.471	0.759	2.13
CS-900-2	0.351	3.415	0.792	2.26
CS-900-3	0.338	3.401	0.811	2.40
CS-900-4	0.337	3.172	0.798	2.36

stack thickness  $L_c$  can be calculated. In addition, the average stacking layer N of graphite microcrystalline can be calculated according to formula (7), and the calculated biochar microcrystalline structure data is shown in Table 3.

$$d_{002} = \frac{\lambda}{2sin\theta_{002}} \tag{4}$$

$$L_a = \frac{1.84\lambda}{\beta_{100} \cos\theta_{100}} \tag{5}$$

$$Lc = \frac{0.90\lambda}{\beta_{002}cos\theta_{002}} \tag{6}$$

$$N = \frac{L_c}{d_{002}} \tag{7}$$

Where  $\lambda$  is the X-ray wavelength used ( $\lambda = 0.154056$  nm);  $\theta_{002}$  is the peak position of peak 002, and  $\theta_{100}$  is the peak position of peak 100 in radians;  $\beta_{002}$  is the half-width of peak 002, and  $\beta_{100}$  is the half-width of peak 100 in radians [32].

The data in Table 3 show that the activation temperature has little effect on d<sub>002</sub>, which remains at about 0.360 nm. d<sub>002</sub> decreased from 0.360 nm to 0.337 nm with the increased activation ratio. The laver spacing of biochar is relatively close to that of graphite, which indicates that the degree of graphitization has been relatively high. The rising activation temperature can increase La from 3.095 nm to 3.471 nm. The activation ratio has the opposite effect of temperature, so La decreases from 3.423 nm to 3.172 nm. The activation temperature has little effect on L<sub>c</sub>, maintained at about 0.760-0.770 nm, while the activation ratio will increase L<sub>c</sub>. In addition, the N of graphite microcrystalline was relatively stable in different temperature ranges, around 2.14 nm. The increase in the activation ratio will increase the number of stacking layers of microcrystals. The change of microcrystalline structure with activation conditions can be seen in Fig. 3-b. In general, the increase in activation temperature makes the graphite microcrystalline structure wider, while adding the activation ratio makes the graphite microcrystalline structure narrower and tighter.

#### 3.3. Elemental and oxygen-containing group analysis

Table 4 shows the C/H/O/N/S element content from elemental analysis(EA) and the surface element content from XPS. EA analysis for both CS-900-3 and CS-900-4 was repeated twice. Combined with the EA

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element analysis results of biomass in Table 1, the C content of biomass increased after carbonization, and the H and O content decreased significantly. Compared with H-biochar, the C content of biochar decreased after activation, and the O content increased to a certain extent. The increase in activation temperature intensifies the reaction of KOH with biochar, creates more defect sites, introduces the O element while consuming the C element, and forms a more oxygen-containing structure, which can be intuitively reflected in the following TPD test results. The content of C decreased from 67.46% to 64.27%, and the content of O increased from 30.04% to 34.01%. With the increase of the activation ratio, the C element showed a trend of first decreasing and then increasing. When the activation ratio was 2:1, the O element content was the highest, at 41.89%. It may be that when the activation ratio exceeds 2:1, the molten KOH content is too high to intercept more volatiles and block the volatile channel, resulting in an increase in C and H content in biochar and a corresponding decrease in O content in biochar [26]. Fig. 4 shows that the O/C change law from EA is consistent with its O-content change law. The H/C ratio shows a trend of decreasing and increasing under different activation temperatures and ratios

Most of the surface O content tested by XPS is lower than those tested by the EA. This is because most of the biochar surface is produced by well-developed micropores inside the biochar (i.e., within the pore channels). Therefore, the O element is not directly probed by XPS, which can explain the difference in oxygen content compared to the EA analysis data. This is similar to the phenomenon studied by Blankenship et al. [[33]] The O content on the biochar surface within 900 °C is always lower than the EA test results, and the values of the two gradually approach as the temperature increases. At 1000 °C, the temperature may be too high, resulting in the destruction of oxygen-containing groups on the surface of biochar so that the O content suddenly decreases. For the CS-900-2, we conducted repeat tests of XPS to avoid accidents in the test. With the increase of the activation ratio, the O content on the biochar surface first decreases and then increases. The O element content on the



**Fig. 4.** O/C ratio and H/C ratio (%) before and after biochar activation, from EA and XPS.

Table	4
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Changes in elemental content of biochar after activation (from EA and XPS, wt%).

0										
	Sample	С	Н	0	Ν	S		С	0	Ν
EA	H-biochar	78.28	1.92	18.80	0.94	0.06	XPS	-	-	-
	CS-700-1	67.46	1.68	30.04	0.77	0.05		81.18	17.56	1.25
	CS-800-1	66.28	1.19	31.87	0.64	0.02		71.00	27.76	1.24
	CS-900-1	66.4	0.96	32.11	0.54	0		67.96	30.91	1.13
	CS-1000-1	64.27	1.02	34.01	0.56	0.15		84.95	13.84	1.21
	CS-900-2	56.86	0.67	41.86	0.6	0.01		80.21	18.58	1.2
	CS-900-3	73.64	0.60	25.19	0.54	0.03		72.48	26.28	1.24
	CS-900-4	76.4	1.14	21.57	0.75	0.14		72.22	26.47	1.31



Fig. 5. (a) XPS curve of biochar and its C1s peak splitting diagram, (b) variation of biochar surface groups under different activation conditions.

Table 5Peak splitting results for C1s.

Sample	Surface concentration from C1s spectra (at.%)					
	С-С, С-Н	С-О, С-ОН	C=O	0=C-0		
CS-700-1	58.59	21.12	6.99	13.25		
CS-800-1	60.83	18.88	7.07	13.11		
CS-900-1	61.91	19.13	7.25	11.84		
CS-1000-1	67.01	15.75	6.66	10.72		
CS-900-2	65.90	15.73	7.27	10.98		
CS-900-3	60.15	17.71	7.80	14.15		
CS-900-4	56.52	20.93	7.24	15.21		

surface gradually exceeds the O content determined by EA. The change law of the O/C ratio on the biochar surface is also consistent with the change law of O-containing elements in its test, as shown in Fig. 4.

The test results of EA and XPS show that the change law of O content inside biochar and surface O content is inconsistent. Therefore, the process of KOH activation biochar to generate oxygen-containing groups is as follows: as the temperature rises, biochar will pull the molten KOH into the inside of the biochar to react. The boiling point of K (762 °C) has not been reached at a temperature of 700 °C, so the biochar surface has not been well activated. When the temperature exceeds 800 °C, the activation effect is noticeable. The oxygen-containing groups on the biochar surface are in a continuous process of "generation-transformation-destruction". A high activation ratio will reduce the amount of oxygen-containing groups. However, when KOH reaches a specific concentration, OH- from KOH can quickly occupy the active vacancy formed by the reaction energy of KOH and biomass into a new O-containing group [25,26].

To further analyze the surface groups of biochar, the measured XPS data and its peak splitting results are shown in Fig. 5. The C and O peaks under different activation conditions showed apparent differences, and the C1s peak was divided into four peaks according to the previous peak splitting method [34,35]. The four peaks of C1s are 284.6, 286.1, 287.5, and 289.1 eV, representing C-C/C-H, C-O/C-OH, C=O, and O-C=O,

respectively, as shown in Fig. 5-a.

Fig. 5-b shows the evolution of surface groups under different activation conditions, and the specific peak-splitting results are shown in Table 5. Hu et al. [26] found the O-C=O group on the surface of biochar replaced the C=O group and became the main O-containing species after introducing KOH. In our study, C-O/C-OH and O-C=O are the main oxygen-containing groups under different activation conditions; C=O groups remain relatively stable, the content fluctuates around 7%-8%, and the change rules of C-C/C-H groups are opposite to C-O/C-OH and O-C=O. The content of C-C and C-H groups increases monotonically with the increase of activation temperature and increases first and then decreases with the addition of activation ratio. C-O/C-OH and O-C=O showed a decreasing trend with the increased activation temperature, and decreased first and then increased with the increase of activation ratio. This is consistent with Pinij et al. [36], the research concludes that increased pyrolysis temperature and KOH catalyst concentration will increase the aromatic hydrocarbon content on the biochar surface. In our study, when the activation ratio exceeds 2:1, KOH reacts with oxygen-containing groups or etches carbon fragments to form active vacancies filled by OH- to create new O-containing species [25,37], as shown in formula (8) [38].

$$OH^{-} + C(vacancies) \rightarrow (C = O) + (-OH) + C - O + (O - C - O) + (-COOH)$$
(8)

The O-containing sites usually affect biochar's adsorption capacity and catalytic activity [39], so we quantitatively characterize the number of C(O) (oxygen-containing complex sites) by TPD, and the results are shown in Fig. 6. Carbon-based materials' C(O) desorption products can be divided into CO and CO<sub>2</sub>. In general, changes in active sites are quantified by analyzing detected CO and CO<sub>2</sub> [33,40]. However, only the generation of CO was seen in this experiment, which may be because the number of C(O) sites related to CO<sub>2</sub> generation in biochar treated by KOH is too small, and the concentration of CO<sub>2</sub> desorbed is too low, which does not reach the accuracy of equipment detection.

Fig. 6-a shows the release process of CO during the programmed heating process: the amount of CO released in the low-temperature



Fig. 6. (a) TPD curve of biochar samples, (b) total amount of C(O) active site desorbed per unit mass, (C) total number of active site and oxygen content change trend.



Fig. 7. Adsorption and desorption curve of hydrogen by biochar at room temperature.

region is small, and the instantaneous release of CO increases significantly as the temperature increases. The activation process affects the properties of the surface complex C(O) and thus acts on its desorption process. And the main desorption differences are manifested in the mesothermal region. The amount of CO released in the mesothermal region will gradually increase with the increase of activation temperature and increase first and then decrease with the addition of activation ratio. Fig. 6-b is the total amount of active sites C(O) for unit mass biochar. Compared with CS-700-1, the number of C(O) increased by 1.03, 1.31, and 1.34 times for every 100 °C increase in activation temperature. When the activation ratio is 2:1, the number of active sites is the largest, and the amount of active sites of CS-900-2 is 1.13 times that of CS-900-1. Fig. 6-c shows that active site C(O) change law positively correlates with the change law of biochar O content.

#### 3.4. $H_2$ storage capacity

Fig. 7 shows hydrogen's absolute adsorption and desorption isotherm from different samples. The hydrogen storage capacity of biochar is determined in the pressure range of 25  $^{\circ}$ C and 0–50 bar. The hydrogen desorption curve almost coincides with its adsorption curve, and the hydrogen adsorbed and stored in the depressurization process is almost entirely desorbed and released. This shows that biochar is mainly physically adsorbed with hydrogen. Therefore, the release conditions of hydrogen do not need to increase the temperature, the hydrogen analysis performance is excellent, and the desorption conditions are

Table 6							
Hvdrogen	storage	capacity	of biocha	r under	different	pressure	s

Samples	H <sub>2</sub> uptake (wt%,1 bar)	H <sub>2</sub> uptake (wt%,10 bar)	H <sub>2</sub> uptake (wt%,30 bar)	H <sub>2</sub> uptake (wt%,50 bar)
CS-700-1	0.01	0.07	0.16	0.23
CS-800-1	0.01	0.08	0.20	0.30
CS-900-1	0.01	0.08	0.20	0.31
CS-1000-1	0.01	0.11	0.24	0.36
CS-900-2	0.02	0.11	0.25	0.37
CS-900-3	0.01	0.11	0.27	0.43
CS-900-4	0.02	0.12	0.32	0.52

#### Table 7

Comparison of hydrogen storage capacity of various materials at room temperature.

References	Materials	Activation method	Hydrogen storage capacity (wt%)	Conditions (Temperature/Pressure)
Pinjari et al.(2023) [41]	MWCNTs	H <sub>2</sub> SO <sub>4</sub> :HNO <sub>3</sub> functionalization	0.149	25 °C/50 bar
Kaskun et al.(2018) [42]	MWCNTs	Ni-doped	0.298	25 °C/20 bar
Helena et al.(2018) [46]	MOF	Ni functionalized	1.23	25 °C/170 bar
Liu et al.(2018) [47]	Carboxylic graphene oxide	TiO <sub>2</sub> composite	1.48	25 °C/5 bar
Bajestani et al.(2016) [48]	graphene oxide	TiO <sub>2</sub> composite	0.39	25 °C/10 bar
Xia et al.(2014) [44]	Activated carbon	Templating technique and CO <sub>2</sub>	0.95	25 °C/80 bar
Stadie et al.(2012) [43]	Zeolite	Polymerization, carbonization	0.46	25 °C/300 bar
Sun et al.(2010) [45]	Corncob	KOH	0.44	25 °C/50 bar
This work	Corn straw	КОН	0.52	25 °C/50 bar

relatively mild.

Table 6 summarizes the absolute hydrogen storage capacity of biochar at different pressures. The biochar surface at room temperature and 1 bar has less contact with hydrogen molecules, resulting in the physicochemical structure characteristics not affecting the hydrogen adsorption, so the amount of hydrogen adsorbed is not significantly different. When the pressure exceeds 10 bar, the pressure difference promotes the diffusion of hydrogen molecules to the inside, the accessible area of hydrogen molecules increases, and the hydrogen adsorption capacity shows apparent differences. The gain of enhanced hydrogen adsorption brought by the increase in the activation ratio is more significant than that obtained by the activation temperature. And as the pressure increases, the gain effect expands further. Compared with CS-700-1, the hydrogen storage capacity at 50 bar increased by 30.45%, 34.78%, and 56.52% for every 100 °C increase. Compared with CS-900-1, the hydrogen storage capacity of biochar at 50 bar increased by 19.36%, 38.71%, and 67.74% with the increase in activation ratio. And the hydrogen adsorption capacity of CS-900-4 at 50 bar can reach 0.52 wt%.

Table 7 compares the hydrogen storage capacity of different materials at room temperature. It is worth noting that the adsorption capacity of CS-900-4 is 0.52 wt% in our work, and it has yet to reach saturation. The hydrogen storage capacity will be further increased under higher pressure conditions, exceeding the hydrogen storage capacity of MWCNTs s<sup>[41, 42]</sup> and Zeolite [43] and also showing certain advantages in porous carbon [44,45]. However, it is much lower than the hydrogen storage capacity of MOF [46] and graphene oxide [47,48] because their additional metal loading enhances hydrogen adsorption. The above analysis shows that biochar has great potential in the direction of hydrogen storage at room temperature.

Based on the Freundlich and Langmuir models, the hydrogen adsorption process of different samples was analyzed, and the isotherm model suitable for hydrogen storage at room temperature was further studied. Table 8 shows the results of the relevant fitting model, and Fig. 8 compares the Freundlich model's fitting results with the experimental results. Combined with Table 8 and Fig. 8, it shows that the Freundlich model can predict the experimental test data well. The fitting result of the Freundlich model is better than that of the Langmuir model (n = 1, 2).

# 3.5. Joint effect of texture and chemical properties on hydrogen adsorption

Our previous work found that the pore structure of biochar at low temperatures  $(-196 \ ^{\circ}C)$  determines hydrogen adsorption, and the chemical structure has little effect [27]. In this work, as shown in Fig. 9, the hydrogen storage capacity at room temperature of the seven biochar samples at different pressures was correlated with their BET area. The correlation was very poor in the low-pressure area, and the effect of the pore structure on hydrogen adsorption gradually increased at elevated



Fig. 8. Biochar hydrogen adsorption and Freundlich (solid) fitting curve.

Table	8
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Models	Parameters	CS-700-1	CS-800-1	CS-900-1	CS-1000-1	CS-900-2	CS-900-3	CS-900-4
Freundlich	k	0.01	0.01	0.01	0.02	0.02	0.02	0.01
	n	1.35	1.26	1.22	1.32	1.28	1.19	1.08
	R <sup>2</sup> (%)	99.89	99.85	99.42	99.30	99.90	99.68	99.93
	Reduced Chi-Sqr	7.55E-6	1.77E-5	6.26E-5	1.15E-4	1.71E-5	6.38E-5	2.07E-5
Langmuir n = 1	Qe	0.53	0.90	0.97	0.78	1.00	1.51	3.87
	KL	0.02	0.01	0.01	0.02	0.01	0.01	0.00
	R <sup>2</sup>	99.72	99.59	99.25	99.66	99.71	99.63	99.91
	Reduced Chi-Sqr	1.77E-5	4.56E-5	7.56E-5	5.35E-5	4.46E-5	6.94E-5	2.61E-5
Langmuir n = 2	Q <sub>e1</sub>	0.76	6.35	1648.14	0.39	0.12	1015.20	5.30
	$Q_{e2}$	0.01	8.76E-4	2.81E-6	0.02	0.08	6.17E-6	0.00
	K <sub>L1</sub>	0.02	0.05	0.09	0.39	560.95	0.15	0.01
	K <sub>L2</sub>	0.47	0.21	0.07	0.02	9.92	0.04	24.14
	R <sup>2</sup>	99.89	99.84	99.334	99.61	99.90	99.66	99.92
	Reduced Chi-Sqr	6.92E-6	1.76E-5	6.67E-5	6.12E-5	1.49E-5	6.38E-5	2.23E-5



Fig. 9. Correlation between hydrogen storage capacity and BET area of biochar at room temperature.

pressure. When the pressure exceeds 30 bar,  $R^2$  does not change much. However,  $R^2$  is 84.84% even at 50 bar, which means the pore structure parameters are not the decisive factor for the hydrogen adsorption of biochar at room temperature. And the hydrogen adsorption process may be controlled by the joint control of the pore and surface chemical structure, which is more evident in the low-pressure area.

It is agreed that the hydrogen storage capacity of carbon-based materials is positively correlated with their specific surface area [45,49-52]. However, considering the influence of oxygen-containing groups, the adsorption characteristics of biochar on hydrogen are coupled with the effect of the two.

We further examine the relationship between hydrogen storage capacity and physicochemical structure at 10 bar, 30 bar, and 50 bar because the hydrogen adsorption of various biochar at room temperature and 1 bar is only approximately 0.01 wt%. The oxygen promotion and inhibition zones are separated by the O content's promotion/inhibition effect on hydrogen adsorption at various pressures, as shown in Fig. 10.

In the oxygen promotion zone, CS-1000-1's specific surface area grew by 43.69% compared to CS-700-1, its oxygen content increased by 13.22%, and its ability to adsorb hydrogen at pressures of 10 bar, 30 bar, and 50 bar improved by 57.14%, 50.00%, and 56.52%, respectively. It can be shown that when the oxygen element content is less than 34.01%, the growth of the oxygen-containing structure enhances hydrogen adsorption by biochar. In the oxygen inhibition region, CS-900-2's specific surface area increased by 68.99% and its oxygen content by 23.08% compared to CS-1000-1. In contrast, the increase in hydrogen adsorption at pressures of 10 bar, 30 bar, and 50 bar was just 0%, 4.17%, and 2.78%, respectively. It means that the oxygen-containing structure inhibits the biochar from adsorbing hydrogen when the oxygen level rises over 34.01% and reaches 41.86%. When CS-900-4 was compared to CS-900-2 in the second oxygen promotion zone, its specific surface area grew by 43.55%, and its oxygen content dropped by 48.47%, and its ability to adsorb hydrogen at pressures of 10 bar, 30 bar, and 50 bar improved by 9.09%, 28%, and 40.54%, respectively.

The following conclusions may be drawn from the quantitative examination of the specific surface area, oxygen content, and hydrogen adsorption capacity. When the oxygen content is less than 34%, the increase in oxygen-containing structure improves hydrogen adsorption by biochar. The action of the oxygen-containing structure manifests as inhibition when the oxygen content rises more. The decrease in hydrogen adsorption capability after the oxygen content of CS-900-3





Fig. 10. Effect of oxygen content on hydrogen adsorption at different pressures.



Fig. 11. Effect of acid groups on hydrogen adsorption at different pressures.

and CS-900-4 falls further supports this assertion. It could be because the over-oxidized carbon material lacks complementary structural elements like pore size, which prevents hydrogen from being absorbed by micropores with the right size due to the steric hindrance effect of internal oxygen-containing functional groups on the surface of the carbon-based material. This effect is more pronounced in narrow pores [22,23].

We have established via the above analysis that oxygen-containing groups have the most significant impact in low-pressure regions. We conclude that the hydrogen adsorption properties of biochar at room temperature are not just affected by the specific surface area and internal oxygen-containing structure because for CS-900-3 and CS-900-4, the hydrogen storage capacity in the low-pressure area is increased less than in the high-pressure zone. Studies have demonstrated that functional groups with acidic oxygen, like carboxyl groups, on the surface of carbon-based materials impact hydrogen adsorption [53,54]. As a result, we combine the hydrogen adsorption capacity under different pressures with the variation in biochar's carboxyl content, as shown in Fig. 11.

Fig. 11 demonstrates that under various pressures when the BET area is less than 1155.04 m<sup>2</sup>/g, the reduction of acidic groups increases hydrogen adsorption by biochar. When the BET area is in the second region (between 1155.04 and 2521.93 m<sup>2</sup>/g), the rising trend of the hydrogen adsorption capacity slows down as the number of acid groups rises. Especially at 10 bar, the hydrogen adsorption capacity remains the same. The above analysis demonstrates that increased BET area will increase hydrogen adsorption capacity. This suggests that the growth of acid groups inhibits the adsorption of hydrogen. As acidic groups increased under various pressure ranges, biochar's ability to bind hydrogen changed (CS-900-4 increased by 0%, 8.00%, and 16.22% compared to CS-900-3, and CS-900-3 increased by 9.09%, 18.52%, and 20.93% compared to CS-900-2), showing that the influence of acidic groups in the low-pressure region was more pronounced and reduced the gain effect of specific surface area and oxygen-containing groups. In the low-pressure area, the inhibiting impact became very apparent. Due to its extensive specific surface area and oxygen-containing structure, which encourage hydrogen adsorption more than the acid group inhibitory effect, CS-900-4 has a higher hydrogen storage capacity than CS-900-3.

Fig. 12 shows the linear fitting results of BET area/O content/acidic surface group and hydrogen adsorption capacity at different pressure intervals. This further proves that the three factors jointly control hydrogen adsorption by biochar at room temperature. The fitting degree of BET area and hydrogen adsorption capacity increases at elevated pressure, and the acid group shows the opposite law. At the same time, the oxygen content of O is always maintained at a high degree of fit. The degree of influence of the three on hydrogen adsorption is as follows: O content > acidic groups>BET area (low-pressure region); O content >BET area > acidic groups (high-pressure region).

#### 4. Conclusions

This study used thermochemical procedures to create biochar with various specific surface areas and oxygen-containing structures. The impacts of biochar's specific surface area, oxygen content, and acidic surface groups on hydrogen storage properties at room temperature were thoroughly examined using advanced characterization methods ( $N_2$  adsorption, SEM, XRD, EA, XPS, TPD, and hydrogen storage tests). The following are the key conclusions:

1. KOH activation develops pores by disrupting the graphite microcrystalline structure of biochar. The graphite microcrystalline structure becomes wider as the activation temperature rises, whereas the addition of the activation ratio causes the structure to become



Fig. 12. Linear relationship between BET area, O content and proportion of surface acidic groups in oxygen promotion zone on hydrogen adsorption in different pressure intervals.

tighter and narrower. The activation ratio has a more significant impact on the development of biochar pores than activation temperature.

- 2. Biochar's oxygen concentration rises from 30.04% to 34.01% as the activation temperature rises. The maximum oxygen content, which was 41.89%, occurred when the activation ratio was 2:1. Hydrogen adsorption is promoted when the oxygen content of biochar rises beyond 34.01%, whereas the surface acid group inhibits it.
- 3. The specific surface area, oxygen-containing structure, and surface acidic groups were discovered to be the controlling factors in the adsorption of hydrogen by biochar at room temperature. The degree of influence on hydrogen adsorption is arranged as follows when the pressure is less than 30 bar: oxygen content > acidic group > BET area. The oxygen content > BET area > acidic groups at pressures greater than 30 bar.
- 4. Biochar has several advantages over carbon-based hydrogen storage materials, with a maximum hydrogen storage capacity of 0.52 wt% at 50 bar room temperature. The process of hydrogen being adsorbed by biochar at room temperature can be reasonably predicted using the Freundlich model.

#### CRediT authorship contribution statement

Lihua Deng: Writing – original draft, Investigation, Data curation, Formal analysis. Yijun Zhao: Funding acquisition, Project administration, Writing – review & editing. Shaozeng Sun: Funding acquisition. Dongdong Feng: Validation. Wenda Zhang: Project administration.

#### **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.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

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