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Experimental investigation into causes of coal surface wettability variation resulting from reaction with $scCO_2$-H_2O

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Abstract: Geological CO_2 sequestration (GCS) can help mitigate global warming and enhance methane recovery from coal beds. However, few studies have linked the effects of CO_2 to surface chemistry changes controlling wetting behavior in deep coal beds. Contact angles (CAs) of CO_2/N_2-high volatile bituminous coal-H_2O systems were measured under different temperatures and pressures. The surface chemistry and physical structure of coals were characterized to investigate changes in physicochemical properties and their relations with wettability after reactions. For N_2 treatment, changes in CAs were insignificant. For gaseous CO_2 treatment, the static CA and the average advancing angle increased slightly. With supercritical (sc) CO_2, both the static and dynamic CAs increased significantly, and θ_{adv} changed to intermediate-wet (92°). Reactions with minerals exposed to $scCO_2$ resulted in greater surface roughness and inhomogeneity, greater contact angle hysteresis and more surface sites occupied by $scCO_2$ rather than H_2O. Increases in hydrophobic functional groups and decreases in hydrophilicity were shown by FTIR spectra, reflecting the shedding of polar oxygen-containing functional groups, reduction of hydrogen bonds, and increasing percentage of hydrocarbons. XRD patterns obtained following $scCO_2$-treatment showed that crystallite growth and molecular polymerization were higher toward graphite-like. The calculated structural parameters of functional groups and crystallites both showed elevated coal rank. Changes in crystallite structure, notably higher carbon content and decreased negative surface charge, are unfavorable for water-wetting. This study contributes to understanding surface chemistry changes responsible for decreased wettability during CO_2-enhanced coal bed methane recovery and GCS in coal reservoirs.

Highlights

(1) Wettability of coal treated by $scCO_2$ changed significantly but not by gas-N_2/CO_2 and scN_2.

(2) Under $scCO_2$ treatment, static contact angle changes stabilized at after 48 hours.

(3) $ScCO_2$ treatment decreased abundance of hydrophilic functional groups.

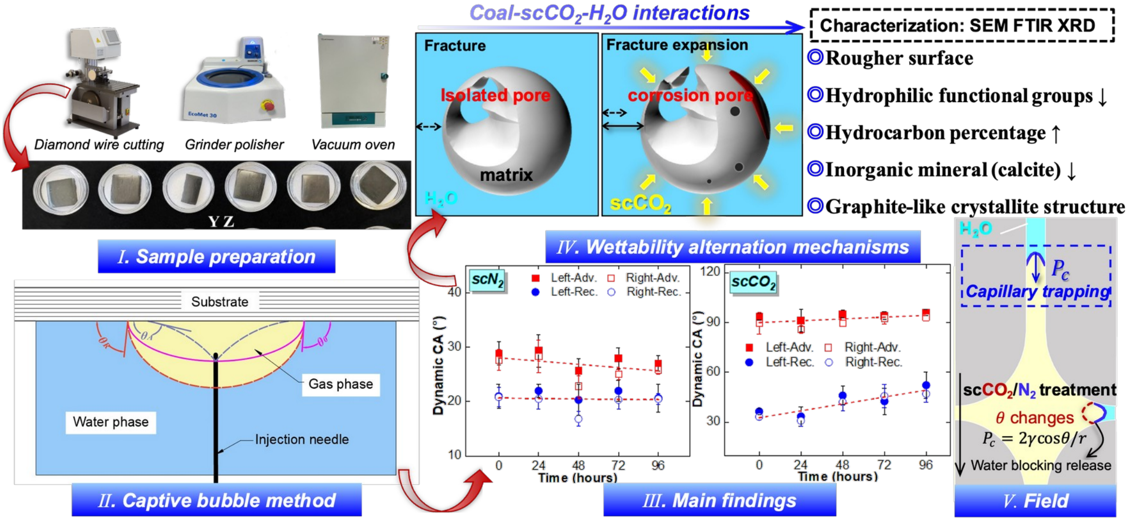
(4) Rougher surface caused by $scCO_2$ treatment generated greater contact angle

hysteresis.

(5) $ScCO_2$ treatment depleted the inorganic minerals in coal (most notably calcite).

Keywords: High volatile bituminous coal; Wetting; Contact angle; Supercritical CO_2; Functional groups; Minerals; Crystallite structure

Graphical abstract



1 Introduction

Geological CO_2 sequestration (GCS) in coal beds provides advantages of CO_2 storage and enhanced coal bed methane recovery (CO_2-ECBM) (Hadi Mosleh et al., 2017). Thus CO_2 enhanced oil recovery (CO_2-EOR) and CO_2-ECBM are widely studied and commercially applied (Godoi and Matai, 2021). CO_2-ECBM has unique advantages resulting from coal matrix micropore development that favors adsorption of CO_2 relative to CH_4 (X. Liu et al., 2023). Thus, adsorption trapping is the most prominent trapping mechanism in coal reservoirs (Iglauer, 2011). Wettability is an important factor which affects the potential and efficiency of CO_2 trapping and methane recovery as shown in **Figure 1** (**Tokunaga et al., 2013**).

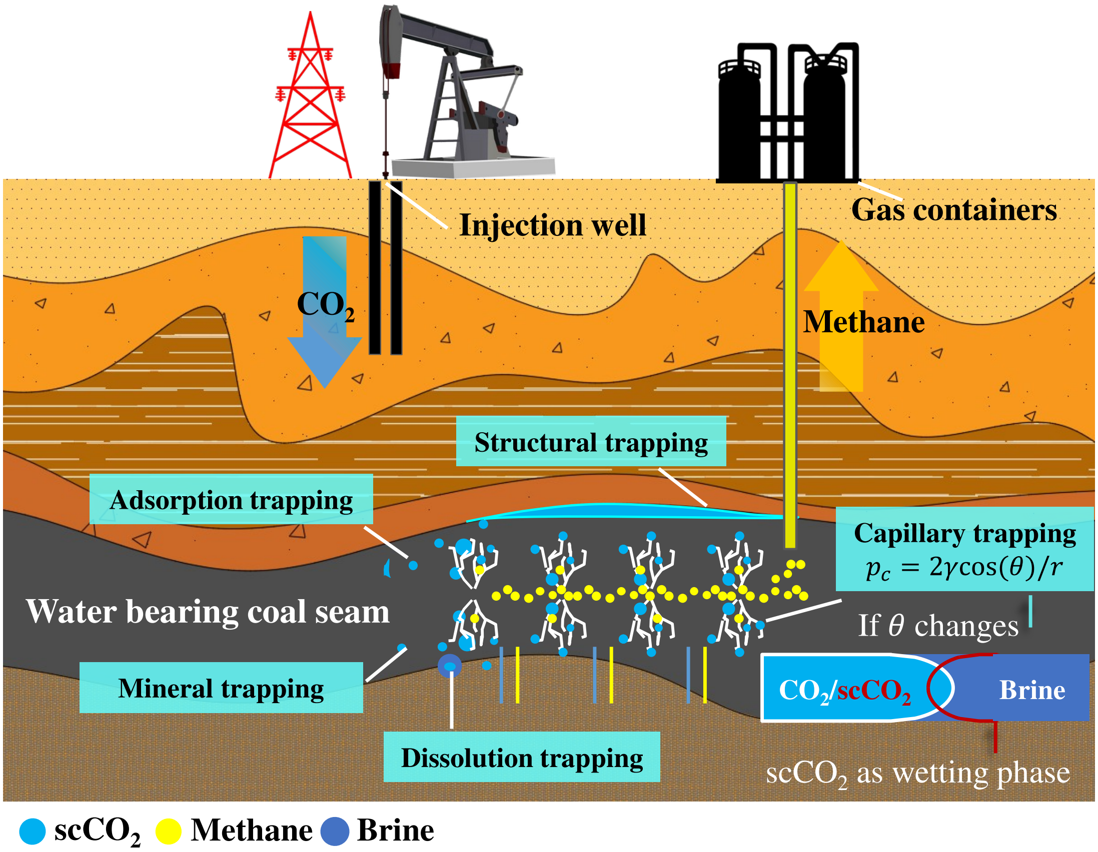


Figure 1 GCS with five main trapping mechanisms and CO_2-ECBM in deep coal reservoirs, where the efficiency of geological storage (especially capillary and structure trapping) and methane recovery displacement depend on wettability.

Minerals show different affinities for H_2O and wettability becomes complicated after CO_2 injection into water-bearing reservoirs (Fatah et al., 2021a). Previous studies reported on the wettability of CO_2-treated minerals (Jung and Wan, 2012; Sun and Bourg, 2023; Tenney and Cygan, 2014), in particular mica (muscovite), quartz or silica, feldspar, calcite, kaolinite, smectite. For coal which is composed of multiple minerals as shown in Table A. 1, wettability is also affected by coal rank and mineral component content (Arif et al., 2016b; Shojai Kaveh et al., 2012), which reflect differences in physicochemical properties of surfaces.

Wettability has been widely investigated as a function of reservoir conditions (temperature, pressure, salinity, ion type/strength, and fluid composition) (Shojai Kaveh et al., 2016, 2011). Arif et al. (2016a) reported that the advancing and receding angles of mica (surface roughness ~12 nm) exposed to CO_2 were positively correlated with pressure and salinity, and negatively correlated with temperature. The advancing contact angle (CA) at 20 MPa and 308 K was ~110°, and water-wet surfaces became CO_2-wet. Iglauer et al. (2012) used molecular dynamics to simulate contact angles in CO_2-H_2O/NaCl-quartz systems as a function of pressure at 300 K and 350 K, and reported that contact angles increased significantly with pressure and weakly with salinity at subcritical and supercritical states. Chen et al. (2015) investigated contact angles of quartz under different ionic strengths (divalent ion Ca^{2+} and monovalent ion Na^+). Ibrahim and Nasr-El-Din (2016) measured the zeta potential of high volatile bitumen coal (hvBb) under different NaCl concentrations by a phase-analysis light-scattering technique. Roshan et al. (2016) conducted experiments under various ion types (NaCl, KCl, $MgCl_2$, $CaCl_2$) and concentrations (0.1, 0.5, and 1 M). Zheng et al. (2020) used nuclear magnetic resonance (NMR) as a non-invasive method to study effects of water status (adsorbed-water, free-water) on wettability, and found that free-water decreased CO_2 wetting and the sensitivity of wettability to pressure.

Previous work explained wettability mainly through influences of molecular density (Arif et al., 2016a), pore adsorption (Sun et al., 2022), interfacial tension, surface charge, and organic matter (Shojai Kaveh et al., 2012). The increase of molecular density implied that the probability of collision increases between H_2O molecules and C molecules (Liu et al., 2010), and H_2O molecules are more likely to be trapped on the surface. Zhu et al. (2019) reported that the dependence of adsorption isotherms on temperature and pressure is consistent with changes in the contact angle. Equilibrium contact angle can be calculated by combining the interfacial tension (IFT) values between different phases with the modified equation of state (EOS) and Young-Laplace equation (Shojai Kaveh et al., 2016). However, while adsorption and interfacial tension are parameters correlated with wettability, it is desirable to identify underlying mechanisms. The reduction of negative surface charge decreases electrostatic repulsions (electric double layer theory (Tokunaga, 2012)), which consequently affects water film stability and wettability. Fatah et al.(Fatah et al., 2021a) reported that $scCO_2$ may dissolve clay and carbonate minerals and transform the clay-rich shale to become CO_2-wet. Arain et al. (2023) reported that trace amounts of hydrocarbons on coal surfaces like dissolved organic matter (Ali et al., 2022) altered wettability of rocks. Crawford et al. (1994) concluded that the effect of oxygen-containing functional groups on wettability cannot be ignored. Gathitu et al. (2009) found that coal exposed to CO_2 may lead to new carbon structure and rearrange macromolecules.

Previous work evaluated wettability of various minerals as a function of reservoir conditions. However, studies on the mechanisms of wettability alteration of coal exposed to $scCO_2$-H_2O are limited, and few have linked wetting behavior with surface chemistry. The surface wettability is complex due to the differences in structure and components between coal and pure, natural minerals. Furthermore, the interactions between coal and CO_2-H_2O also affect the wettability. Wettability variations introduce a large uncertainty into the prediction of trapping CO_2, methane displacement capacity, CO_2 storage height, and CO_2 containment security. Therefore, it is crucial to determine the potential effects of chemical reactions on wettability and the changes in physical structure (porosity, roughness) and surface chemistry (functional groups, crystal structure) of coal surface.

In this work, we measured in-situ static/dynamic contact angles of high volatile B bituminous (hvBb) medium rank coal under N_2/CO_2 treatment at different temperatures, pressures, and exposure times to determine the extent to which changing these conditions alter wettability. We then analyzed physicochemical properties via characterization methods (FTIR, XRD, SEM) in order to identify underlying surface processes responsible for wettability alteration. This study provides measurements-based theoretical guidance for field practices, including the choice of solvents or nanofluids injected to improve CO_2 trapping, and further deepens the understanding of wetting behavior to enhance CO_2-ECBM and GCS.

2 Experiments

2.1 Experimental method and materials

2.1.1 Coal sample and preparation

A high volatile B bituminous (hvBb) medium rank coal was collected from Yuanzhuang (YZ) coal mine in Huaibei, China. The proximate analysis of coal samples is shown in **Table 1**. The coal samples were prepared by block-cutting method, i.e., large coal blocks were cut into smaller square slices with dimensions of ~21mm×21mm×3-4mm (thickness), and then coal surfaces were ground and polished. Some prepared coal samples are shown in **Figure 2a**.

Coal surfaces were polished with a series of silicon carbide sandpapers (220-3000 grit). Small scratches were first removed with 220-320 grit sandpapers, followed by careful water polishing with 400-3000 grit sandpapers to complete the sample surface preparation. We used deionized water to reduce surface charge interference. Sample surfaces were finally cleaned with AccuDuster III 2510 before experiments.

Table 1 Proximate analysis results of coal sample.

Coal sample	M_{ad} (%)	A_{ad} (%)	V_{daf} (%)	FC_{ad} (%)	Coal type
YZ	2.58	9.16	36.75	57.46	hvBb coal

Note: M_{ad}—the moisture content on air-dried basis, A_{ad}—the ash content on air-dried basis, V_{daf}—the volatile matter content on dry-ash-free basis, FC_{ad}—the fixed carbon content on air-dried basis.

2.1.2 Contact angle measurement

Dynamic and static contact angle (CA) measurements are commonly measured by three main methods: sessile drop (Drelich, 2013), pendant drop (Bhutani et al., 2012), and captive bubble (Chau, 2009). We used the captive bubble method to measure CAs (**Figure 2b**), where bubbles were captured beneath a solid substrate submersed in the aqueous phase under precise control of P/T (Wan et al., 2014). Due to surface heterogeneity of substrates, we measured advancing/receding angles (θ_A ¿ θ_R) on both the left and right sides as shown in **Figure 2b**. The CAs reported in this study were all water contact angles, which are measured between the solid-water and nonaqueous fluid-water interfaces. After a bubble captured by the coal substrate separated from the injection needle, we began to photographically record images, which were later processed with Image J to measure static CAs.

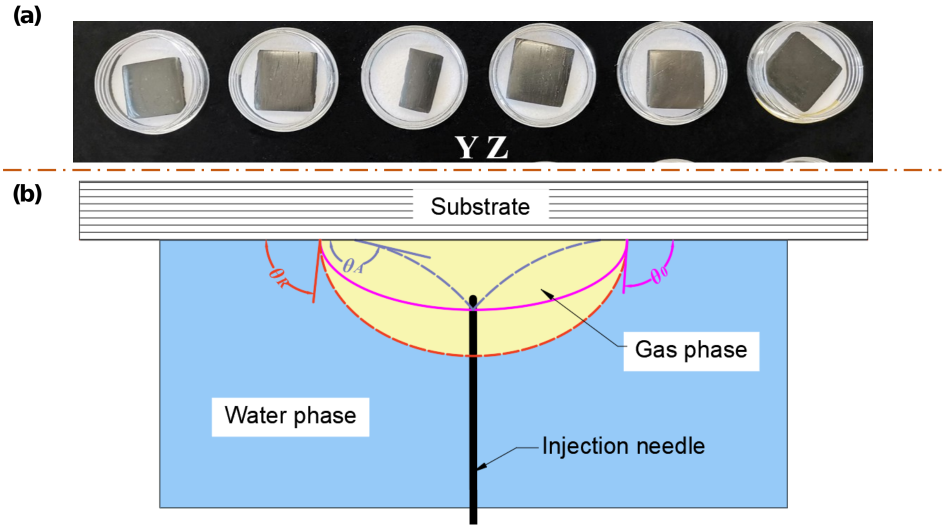


Figure 2 Experimental samples and contact angle measurement. (a) Polished YZ coal samples, (b) Schematic of contact angle measurement by the captive bubble method. Young's equilibrium contact angle ¿θ_0, advancing contact angle ¿θ_A, receding contact angle ¿θ_R. Usually, $\theta_A > \theta_0 > \theta_R$, thus θ_0 is constrained by θ_A and θ_R.

2.2 Experiment setup and procedure

2.2.1 Experiment setup

The experimental system shown in **Figure 3** includes: a high pressure and temperature (P-T) chamber, stirred reactor, pressure control unit (pump, gas cylinder), temperature control unit (temperature controller, thermocouple, heat lamp, circulation fan, and thermal insulation), and experimental information acquisition unit (camera, computer, and light illuminator).

The high P-T viewing chamber (IFT-10, Core Laboratories) can support a maximum working pressure and temperature of 690 bar and 450 K, respectively. An inlet in the upper portion of the chamber is connected to a two-stem manifold (A), one of which is connected to an exhaust pipe to safely vent CO_2 into the ventilation ducts, and the other is connected to a pump (A) that provides back pressure. The bottom of the viewing chamber has two inlets, one of which is connected to a needle valve to generate CO_2 bubbles. The needle valve is connected to pump (B) via a three-way valve for controlling the flow rate of CO_2. The other inlet is connected to a two-stem manifold (B) which connects a stirred reactor and a water tank.

Coal samples are placed on a stainless-steel plate near the upper center of the viewing chamber. Two glass windows that are resistant to high temperature and pressure are installed on opposite sides of the chamber to enable transmission of the illuminator's light into the chamber for recording images of the droplets. The entire experimental system is enclosed in a thermally insulated box to maintain a constant temperature regulated by a temperature controller.

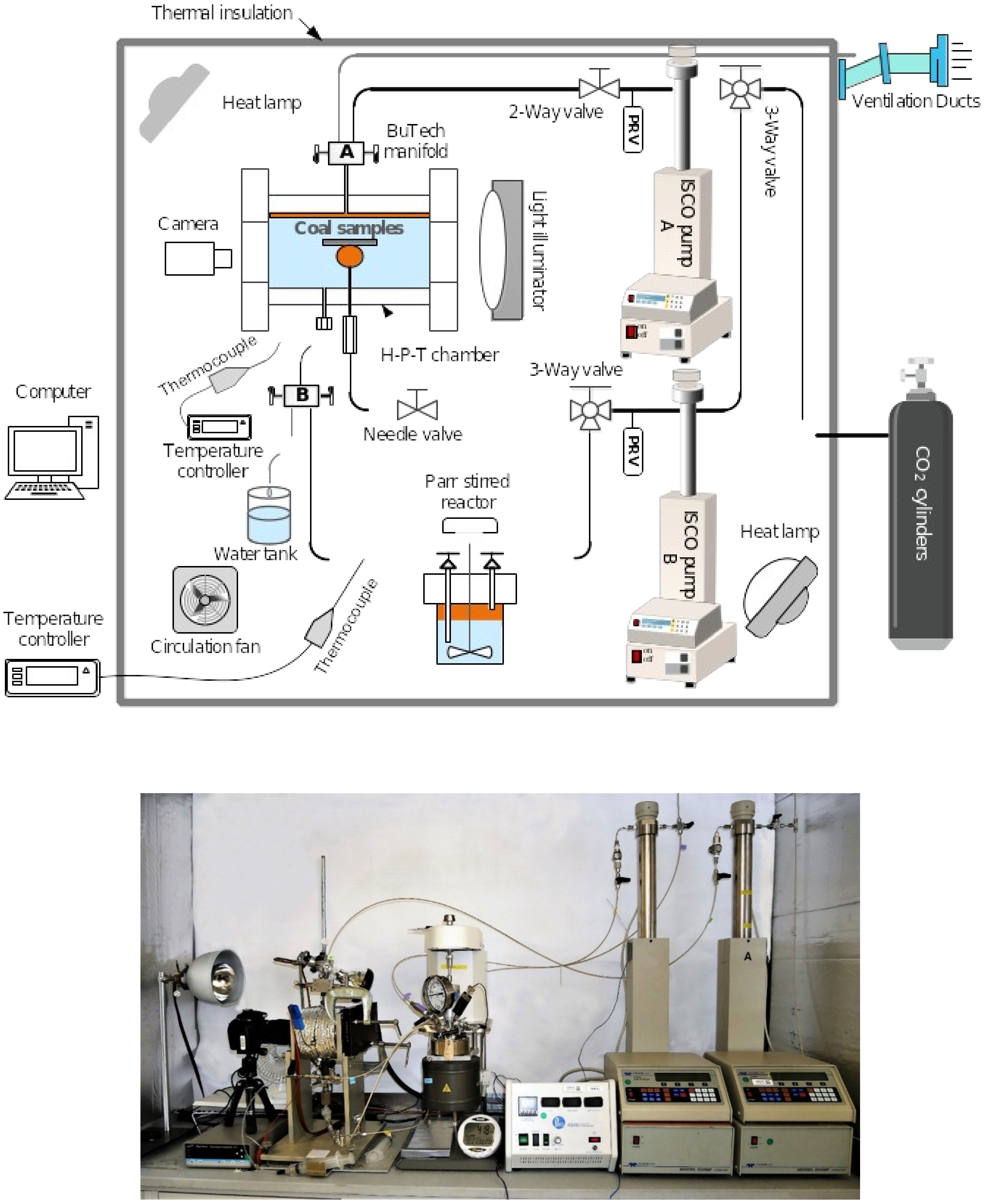


Figure 3 Schematic diagram of the experimental system and photograph of the experimental setup for contact angle measurements.

2.2.2 Contact angle measurement procedures

(a) Preparation before CO_2 releasing. We clamped a coal substrate onto the lower surface of a stainless-steel plate, and then immersed it in high pressure deionized water (20 bar) for a minimum of 48 hours to fill its pores with water. The thermally insulated box and viewing chamber were then heated to the desired temperature. The viewing chamber was pressurized to the desired pressure using pump (A) with CO_2.

The reactor was equilibrated to fully dissolve CO_2 in water, then further stirred for 30 minutes in preparation for transfer of CO_2-saturated water into the viewing chamber. The two pumps were set to a constant pressure difference between injection pressure and back pressure. We then opened the valve between the stirred reactor and the viewing chamber to allow CO_2-saturated deionized water to flow into the chamber and displace the original water. Solubility equilibrium was again established for more than 1 hour.

(b) CO_2 captured by coal substrate. CO_2 bubbles were released from the stirred reactor through the needle valve and captured upon buoyant contact against the overlying coal substrate. In order to measure dynamic contact angles, the CO_2 bubbles advanced through the pressure difference between the reactor and the viewing chamber, and receded through lowering the pressure of the pump (B). The rate of expansion and contraction of the bubbles was controlled with the needle valve.

After each measurement, the pressure chamber was tilted to remove the captured CO_2 bubbles from the substrate. After a period of reaction, new CO_2 bubbles were then released at the same position after dissolution equilibrium. More detailed experiment procedures can be found in our previous work (Zhu et al., 2019).

2.3 Characterization methods of physicochemical property

(1) Surface functional group

The surface functional group chemistry of coal surfaces was measured by Fourier Transform Infrared spectroscopy (FTIR) using VERTEX 80v (Germany, Bruker) as shown in **Figure 4a**. The measurement was conducted by attenuated total reflection (ATR).

(2) Coal surface micromorphology

Surface micromorphological of the coal samples was characterized by scanning electron microscopy (FEI Quanta TM 250, **Figure 4b** with a magnification of 6–100 million and an accelerating voltage of 0.2–30 kV).

(3) Crystallite structure

Coal is a long-range disordered and short-range ordered amorphous crystal. Information on the size, shape, and structure of the ordered crystallite structure can be calculated by diffraction intensity and diffraction angle. The samples were dried to remove water in a vacuum oven before characterization. Crystallite structures of coal were then determined by X-ray diffraction (XRD, Bruker, D8 Advance, **Figure 4c**).

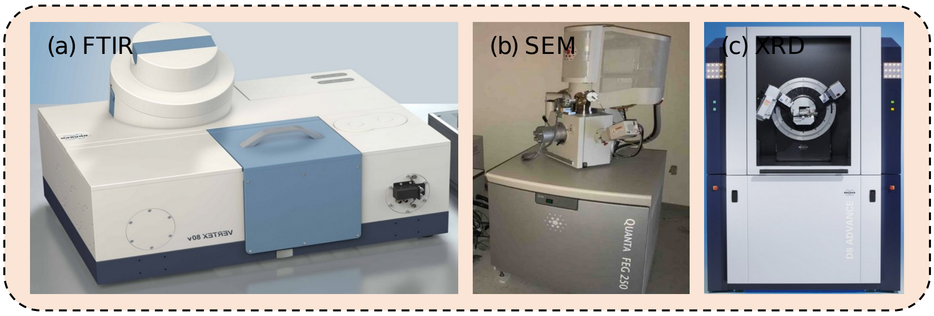


Figure 4 Experimental setup for the characterization of physicochemical properties. (a) VERTEX 80v FTIR; (b) FEI Quanta TM 250 SEM; (c) D8 Advance XRD.

2.4 Experiment design

Factors affecting wettability of coal include physical and chemical properties of coal (mainly surface functional groups and mineral components) and environmental conditions (temperature and pressure). In the process of CO_2 injection into water-bearing coal seams for storage or methane displacement, high pressure or chemical reaction may impact the physical and chemical structure of coal surfaces, and thereby affect the wettability of coal.

In this study, wettability changes over time were measured following coal exposure to low pressure (gaseous) and high pressure (supercritical) CO_2. Due to the poor water solubility of CO_2 under low pressure conditions, its impact on the physical and chemical properties of the coal surface may be not significant, but under high pressure conditions, CO_2 dissolved in water will form an acidic solution, which may have a greater impact on the physical and chemical properties of coal surface. N_2 (the most chemically stable of the known diatomic molecules) is much less soluble in water, so the chemical reaction between its aqueous solution and coal is negligible. Therefore, we also measured the wettability variation of coal surfaces exposed to N_2 under the same experimental conditions, in order to determine the influence of coal reaction with CO_2 aqueous solutions on wettability. The specific experimental conditions are shown in **Table 2**.

Table 2 Experimental conditions.

Type	Critical point	Gas phase	Supercritical phase
N_2	P=34.0 bar, T=−147.0°C	~23°C, 20 bar	45°C, 120 bar
CO_2	P=73.8 bar, T=31.2°C	~23°C, 20 bar	45°C, 120 bar

3 Results

3.1 Coal-N_2-H_2O competitive wetting

Figure 5 gives time-dependent dynamic contact angles for N_2-H_2O-coal systems (values are given in **Table A.3** and **Table A.4**). For gaseous N_2 (P=20 bar, T=25°C), the average advanced (θ_{adv}) and receding (θ_{rec}) contact angles are 28~32° and 22~23.5°, respectively, indicating strong water-wetting. The variation of contact angles was less than 5°, indicating that time-dependent wettability of coal in gaseous N_2-H_2O-coal systems is stable under low pressure. For scN_2 (P=120 bar, T=45°C), the θ_{adv} (24.5~28.5°) and θ_{rec} (18.5~21.5°), also changed very slightly and were close to values under low pressure due to slight variation of density (Zhu et al., 2019). The static contact angles for gaseous N_2 and scN_2 are 23~25° and 22~24°, respectively, which follow similar trends as dynamic contact angles, as shown in **Figure 6**.

Gas or supercritical N_2 is relatively insoluble in water and cannot form acid solution that react with coal under the current experimental condition. The calculated solubility of N_2 in water is ~9.76×10^{-5} mol/mol at 120 bar and 45°C (Battino et al., 1984). Therefore, the only factor that may affect wettability is the high pressure. The applied high pressure is expected to change pore structure of coal (such as pore compaction, pore expansion) or generate fractures (Jia et al., 2022; Wang et al., 2022). However, based on the results of time-dependent dynamic and static contact angles, these physical changes of coal surface caused by high pressure N_2 did not have a significant effect on wettability.

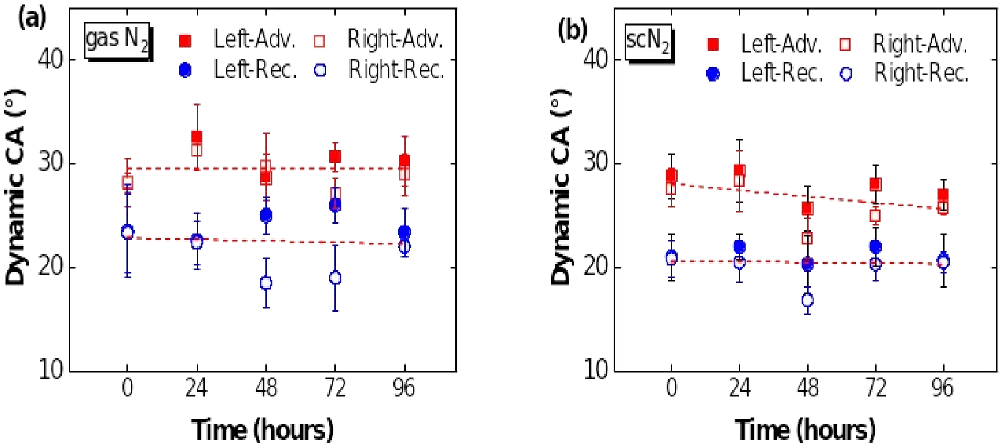


Figure 5 Time-dependent dynamic CAs with N_2 treatment. (a) Dynamic contact angle under gaseous N_2 (P=20 bar, T=25°C), (b) Dynamic contact angle under scN_2 (P=120 bar, T=45°C). "Left-Adv" and "Right-Adv" refer to the advancing contact angles measured on the left and the right side of bubbles, respectively.

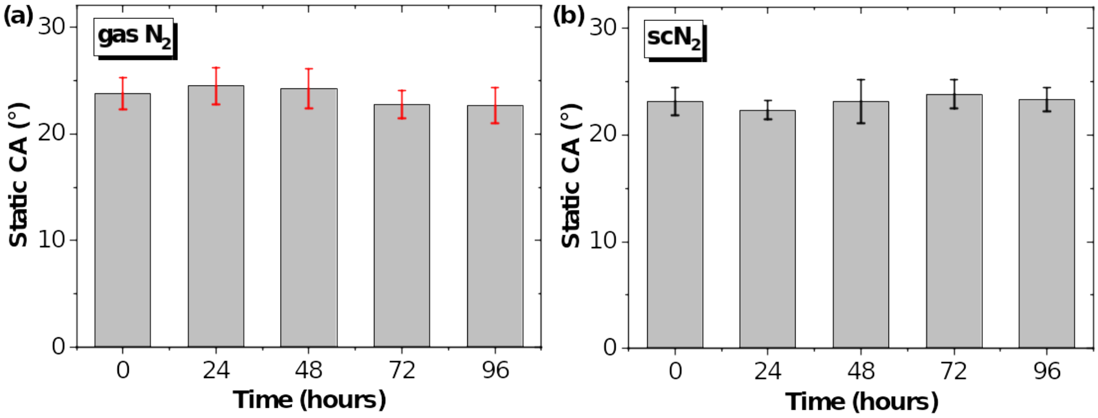


Figure 6 Time-dependent static CAs. (a) Static contact angle under gaseous N_2 (P=20 bar, T=25°C), (b) Static contact angle under scN_2 (P=120 bar, T=45°C).

3.2 Coal-CO_2-H_2O competitive wetting

The time-dependence of dynamic contact angles (CAs) exposed to gas and supercritical CO_2-H_2O systems are presented in **Figure 7**. For gaseous CO_2, the average advancing contact angles (θ_{adv}) varied from 34.1° to 45.7°. The dynamic CA at 0 hour was the highest (with an average value of 45.7°), followed by θ_{adv} decreasing with time. However, dynamic advancing CAs for gaseous CO_2 varied little (~5.3°) from 24 hours to 96 hours, and average receding contact angles (θ_{rec}) changed slightly (19° to 24°). In contrast, for scCO_2, both θ_{adv} and θ_{rec} show obvious increases over time, especially for the θ_{rec} which increased from 35° (0 hour) to 50° (96 hours). The

θ_{adv} with $scCO_2$ changed from water-wet to intermediate-wet.

We also measured the time-dependence of static contact angles (CA) as shown in **Figure 8**. Average static CAs in gaseous CO_2 fluctuated between 22° and 26°, while those in $scCO_2$ increased dramatically from 35° (0 hour) to 56° (96 hours). Additionally, the static CA in $scCO_2$ tends to be stable after 48 hours of reaction. The greater CA after $scCO_2$ treatment is attributed to decrease in pH and more extensive mineral reactions, as will be discussed in section 4.1. The increases in CA with decreasing pH in carbonate solution is consistent with a previous report (Chaturvedi et al., 2009) (4<pH<7) as shown in **Figure 9**.

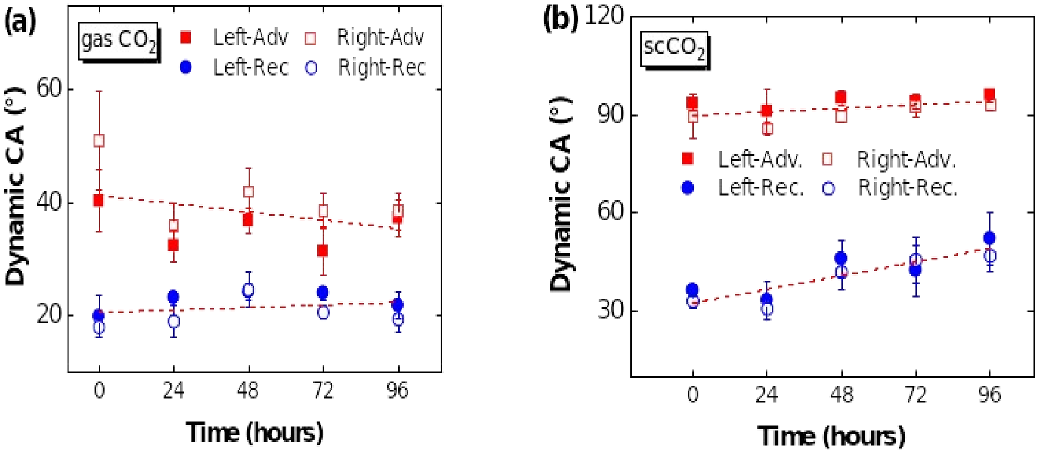


Figure 7 Time-dependent dynamic contact angles with CO_2 treatment. (a) Dynamic CA under gaseous CO_2 (P=20 bar, T=25°C), (b) Dynamic CA under $scCO_2$ (P=120 bar, T=45°C).

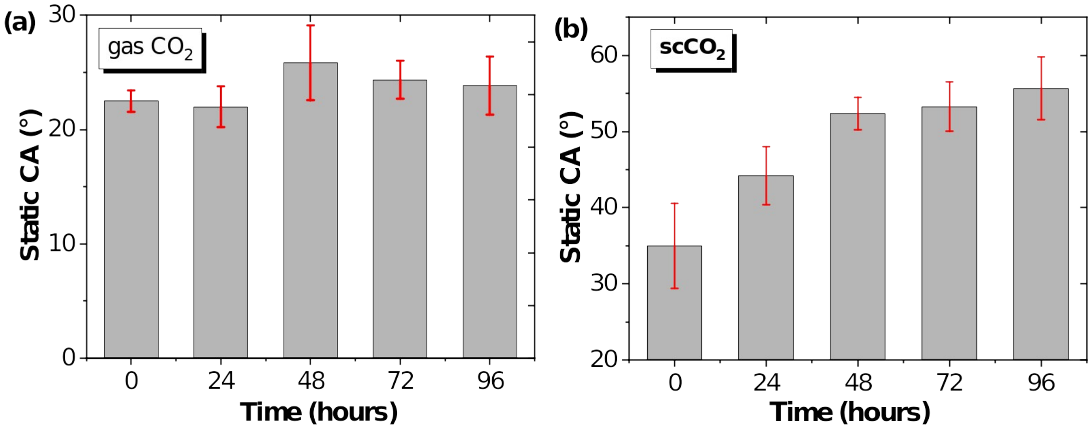


Figure 8 Time-dependent static contact angles. (a) Static CA under gaseous CO_2 (P=20 bar, T=25°C), (b) Static CA under $scCO_2$ (P=120 bar, T=45°C).

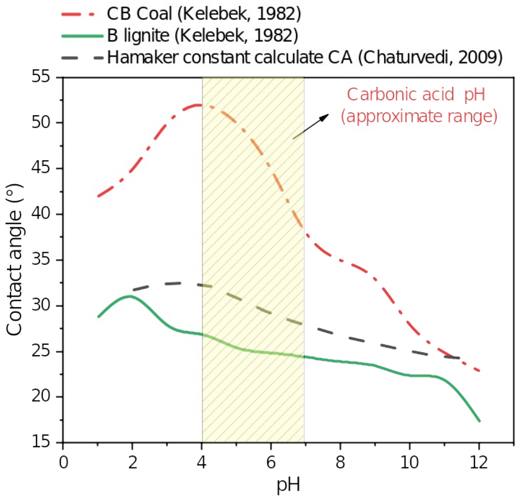


Figure 9 Experimental and calculated contact angles of CB coal and B lignite coal samples with pH (Kelebek, 1982), and calculated CA (Chaturvedi et al., 2009). pH depends on solute concentration and ionization equilibrium constant in the solution, and the pH of carbonic acid usually ranges from 4–7 (MacInnes and Belcher, 1933).

4 Discussion

4.1 Coal surface micromorphology

The coal-scCO_2-H_2O interaction affects wettability through three main physicochemical mechanisms shown in **Figure 10a**. Surface roughness has a potential effect on specific surface area and surface free energy, which consequently affects wettability (Wei et al., 2022). After scCO_2 treatment, the appearance of corrosion pores, connecting partially isolated pores, fracture extension, and edge warping in **Figure 10b** changed surface roughness and pore structure, which resulted from chemical reactions between minerals and the weakly acidic solution. CO_2 dissolved in water produces$H^{+¿¿}$ and $HCO_3^{-¿¿}$ ions in acidic systems (Lerman and Mackenzie, 2018) as shown in Eq.(1). These ions, along with H_2O and CO_2 molecules, altered the mineral composition (mineral composition of raw coal as shown in **Table A. 1**) through reaction Eqs.(2)–(5) (Ao et al., 2017; Labus and Bujok, 2011). The dissolution of the minerals, especially hydrophilic clay and carbonate minerals, has been also reported in previous studies (Fatah et al., 2021b; Lu et al., 2021). The brownish-yellow substance in **Figure 10b** is FeO(OH), which was produced by Fe oxidation of ferrous carbonate to FeO(OH) in the carbonic acid solution.

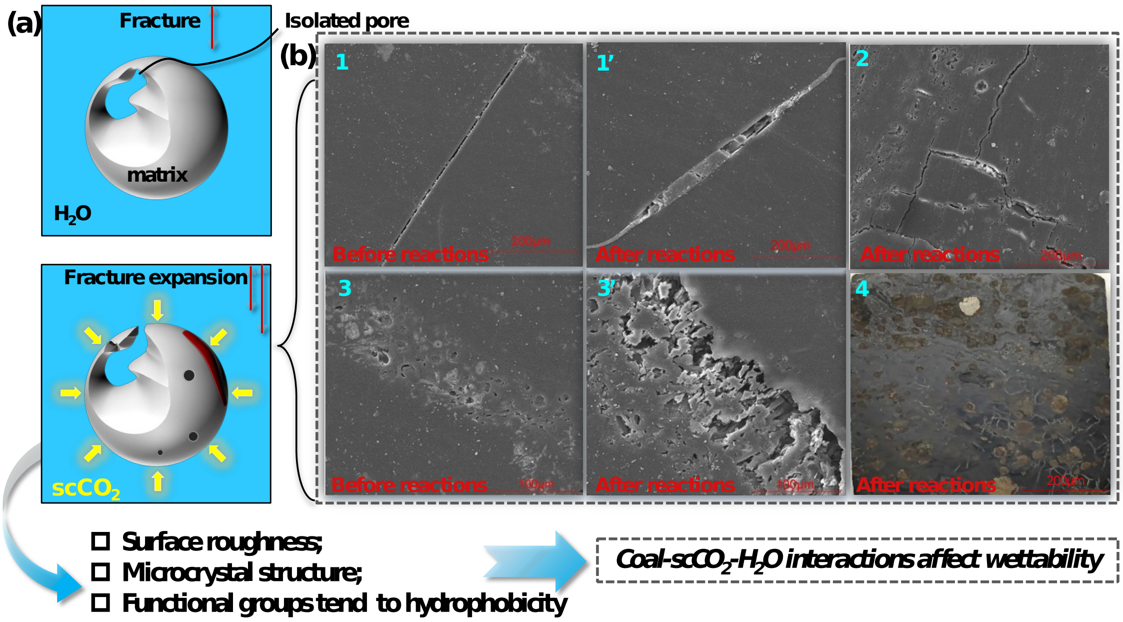


Figure 10 The changes of physicochemical property exposed to scCO$_2$. (a) Schematic diagram of three mechanisms for the effect of coal-scCO$_2$-H$_2$O interactions on wettability. (b) Coal surface micrographs: (1–1') fracture extension before and after reactions with scCO$_2$; (2) edge warping after reactions with scCO$_2$; (3–3') corrosion pores and connection of isolated pores before and after reactions with scCO$_2$; (4) brownish-yellow FeO(OH) after reactions with scCO$_2$. Note: Some of the micrographs in Figure 10 (b) served as the basis for drawing the mechanism schematic in our recently published paper (S. Liu et al., 2023).

$$CO_{2(aq)} + H_2O \Leftrightarrow H^{+\text{¿}+HCO_3^{-\text{¿¿}}\text{¿}} \tag{1}$$

$$\underset{\text{Calcite}}{CaCO_3} + CO_2(aq) + H_2O \Leftrightarrow Ca^{2+\text{¿}+2\,HCO_3^{-\text{¿¿}}\text{¿}} \tag{2}$$

$$Al_2Si_2O_5\text{¿} \tag{3}$$

$$\underset{Dolomite}{CaMg\left(CO_3\right)_2} + 2H^{+\text{¿}\Leftrightarrow Ca^{2+\text{¿}+Mg^{2+\text{¿}+2HCO_3^{-\text{¿¿}}\text{¿}}\text{¿}}\text{¿}} \tag{4}$$

$$\begin{gathered} K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}\text{¿} \\ 0.6\,KAl_3Si_3O_{10}\text{¿} \end{gathered} \tag{5}$$

Additionally, adsorption sites of coal surface increased after reaction with scCO$_2$ since surface fractures are developed and connected (Chen et al., 2019). The higher concentration of CO$_2$ molecules convert some H$_2$O-occupied sites to CO$_2$-occupied sites (Yu et al., 2022), partially displacing the adsorbed water and transforming the coal surface into a heterogeneous surface comprising of solid and CO$_2$-occupied pockets (Sun et al., 2022). The adsorption and interaction energy of CO$_2$ molecules are enhanced in the supercritical state on the coal surface (Liu et al., 2010), which causes CO$_2$ to accumulate as a thin film at the solid/liquid interface (Iglauer et al., 2012; Xu et al., 2023). The chemical reactions of minerals resulted in a rougher coal surface which promotes CO_2 adsorption, and this interfacial behavior favors CO_2-wetting (Zhou et al., 2022).

Contact angle hysteresis, or the difference between θ_{adv} and θ_{rec} denoted by $\Delta\theta$, results from variation of surface roughness, chemical inhomogeneity, and pinning effects (Cai and Song, 2021; Kulinich and Farzaneh, 2009). The average $\Delta\theta$s of coal for gaseous N_2 and scN_2 treatment were 7.0° and 6.3° as in **Figure 11a**, respectively, which were obviously smaller than those of coal for CO_2 treatment as shown in **Figure 11b**. The average $\Delta\theta$ of coal was 16.8° for gaseous CO_2 treatment, while it increased to 52.6° for $scCO_2$ treatment. The mole fraction of CO_2 solubility in water ranges from 0.695×10^{-3} in the gaseous state (T=20°C, P=1 bar) to 2.51×10^{-3} in the supercritical state (T=50°C, P=85.1 bar) (Sabirzyanov et al., 2002). Differences in $\Delta\theta$ indicate that chemical reactions resulted in greater surface inhomogeneity of coal after reaction with $scCO_2$.

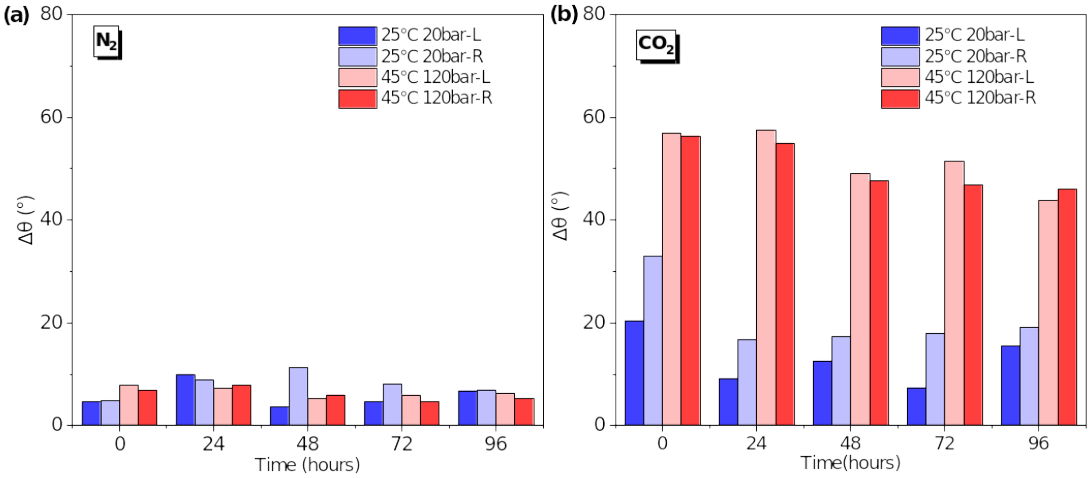


Figure 11 Contact angle hysteresis denoted by $\Delta\theta$ with time for CO_2 and N_2 treatment under different pressures and temperatures, respectively. "L" and "R" refer to CA measurements on the left and the right side of bubbles, respectively.

4.2 FTIR functional groups

Surface roughness mainly reflects physical structure, and the influence of surface chemistry (functional groups, crystallite structure) on wettability also needs to be further discussed. The FTIR spectra of coal are usually divided into four absorption bands (Lu et al., 2021), i.e., hydroxyl groups (3700–3200 cm^{-1}), aliphatic hydrocarbons (3000–2800 cm^{-1}), oxygen-containing groups (1800–1000 cm^{-1}), and aromatic hydrocarbons (900–700 cm^{-1}). The assignment of functional groups in each absorption band is shown in **Figure 12a**. **Figure 12b** gives FTIR spectra of raw coal, and coal with H_2O treated by scN_2 or $scCO_2$ at T=45°C and P=90 bar after 96 hours, respectively. Absorption peaks of three group experiments had similar peak shape but different peak intensity and area, indicating that the content of functional groups changed but types of functional group and macromolecular structure remained basically similar (Shang et al., 2021). Due to the influence of algorithms, samples, and setups, absorption peaks in the same band could still be shifted and overlapped (Wang et al., 2017). Previous studies disputed assignment of different peak positions to the same functional group (Yan et al., 2020), so we used integral areas of sub-peaks rather than peak intensity to determine types and content of functional groups. The fitted curves were decomposed into sub-peaks controlled by Gaussian or Lorentz algorithms with the correlation coefficient $R^2 > 0.98$.

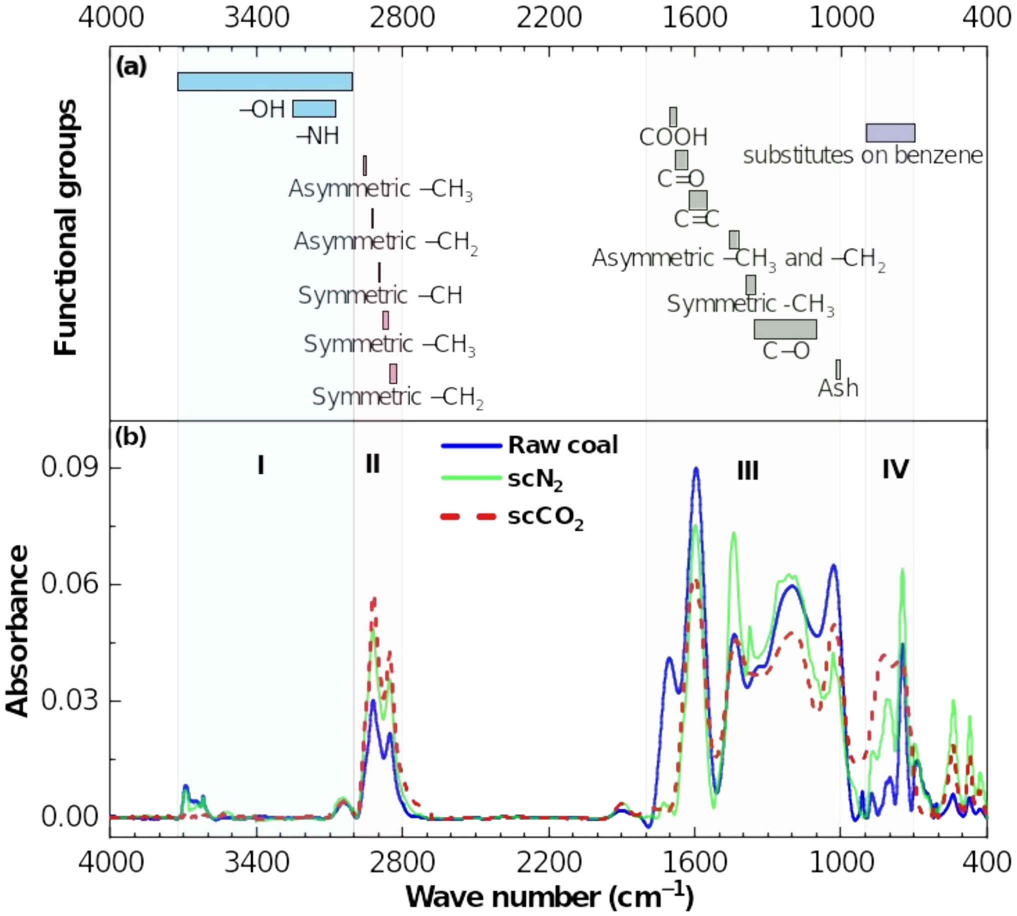


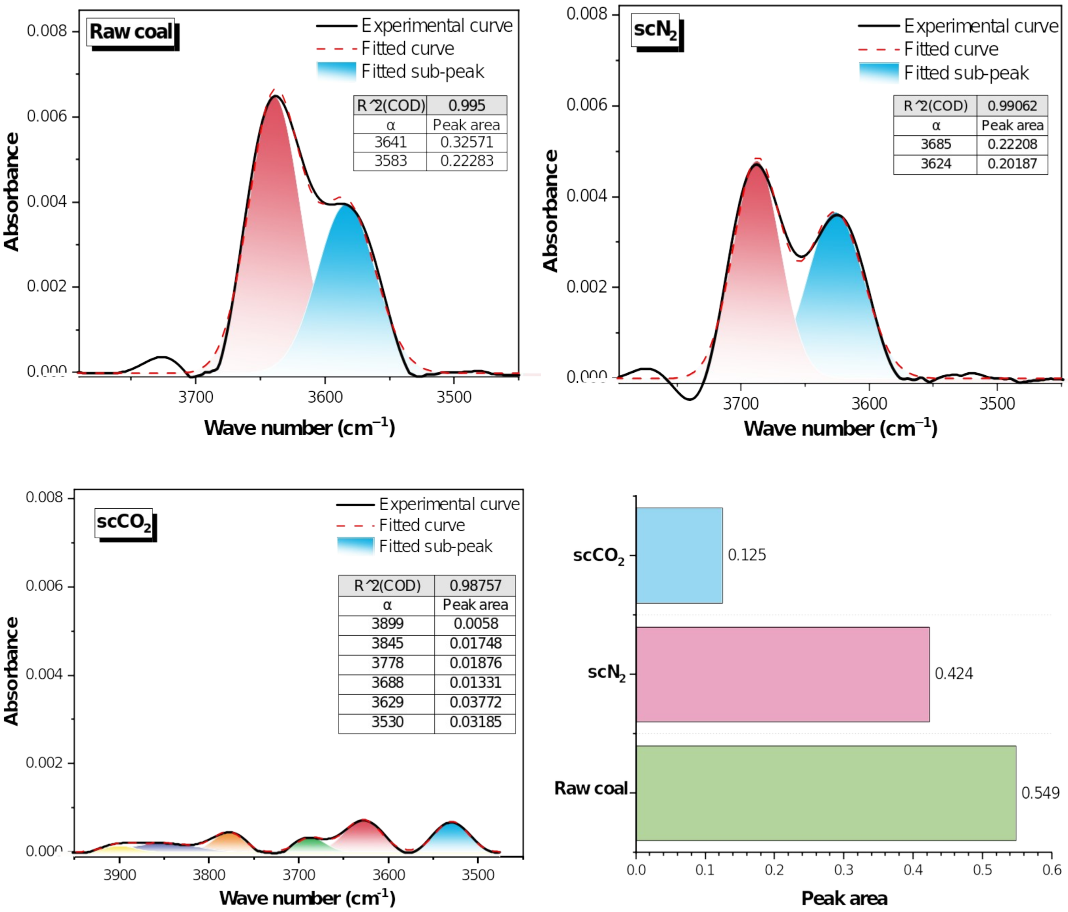
Figure 12 The FTIR spectra and assignment of functional groups. (a) Assignment of functional groups of coal surface in the range of 4000–400 cm^{-1}. (b) The FTIR spectra of raw coal, scN_2, and $scCO_2$ were divided into four absorption bands: Ⅰ—Hydroxyl groups, Ⅱ—Aliphatic hydrocarbons, Ⅲ—Oxygen-containing groups, Ⅳ—Aromatic hydrocarbons.

(1) Hydroxyl functional groups

The absorption peaks in the range of 3700–3200 cm^{-1} are mainly generated by stretching vibration of –OH, which is the main functional group for the formation of hydrogen bonds. As shown in **Figure 13**, absorption peaks appeared in the range of 3650–3400 cm^{-1}, and main types of hydroxyl groups are OH–π, OH–OH, and free–OH.

The peak shape of coal for $scCO_2$ treatment was different from that of raw coal and coal for scN_2 treatment in **Figure 13**, and all of the sub-peak intensities of coal for

$scCO_2$ treatment were below 0.001. The integral areas of sub-peaks of hydroxyl groups for coal with H_2O treated by $scCO_2$, scN_2 and raw coal were 0.125, 0.424, and 0.549, respectively. The reduction of hydroxyl groups decreases the number of hydrogen bonds between H_2O molecules and C atoms of coal (Besford et al., 2020), whereas intermolecular forces (van der Waals) between CO_2 molecules and coal C atoms become prominent. Thus the adsorption potential of CO_2 on coal increases significantly ("Surface physical properties and its effects on the wetting behaviors of respirable coal mine dust," 2013). Water films on the surface were displaced by CO_2 dissolved in water, and water-wet surfaces changed to be intermediate-wet or CO_2-wet.



R^2(COD)	0.995
α	Peak area
3641	0.32571
3583	0.22283

R^2(COD)	0.99062
α	Peak area
3685	0.22208
3624	0.20187

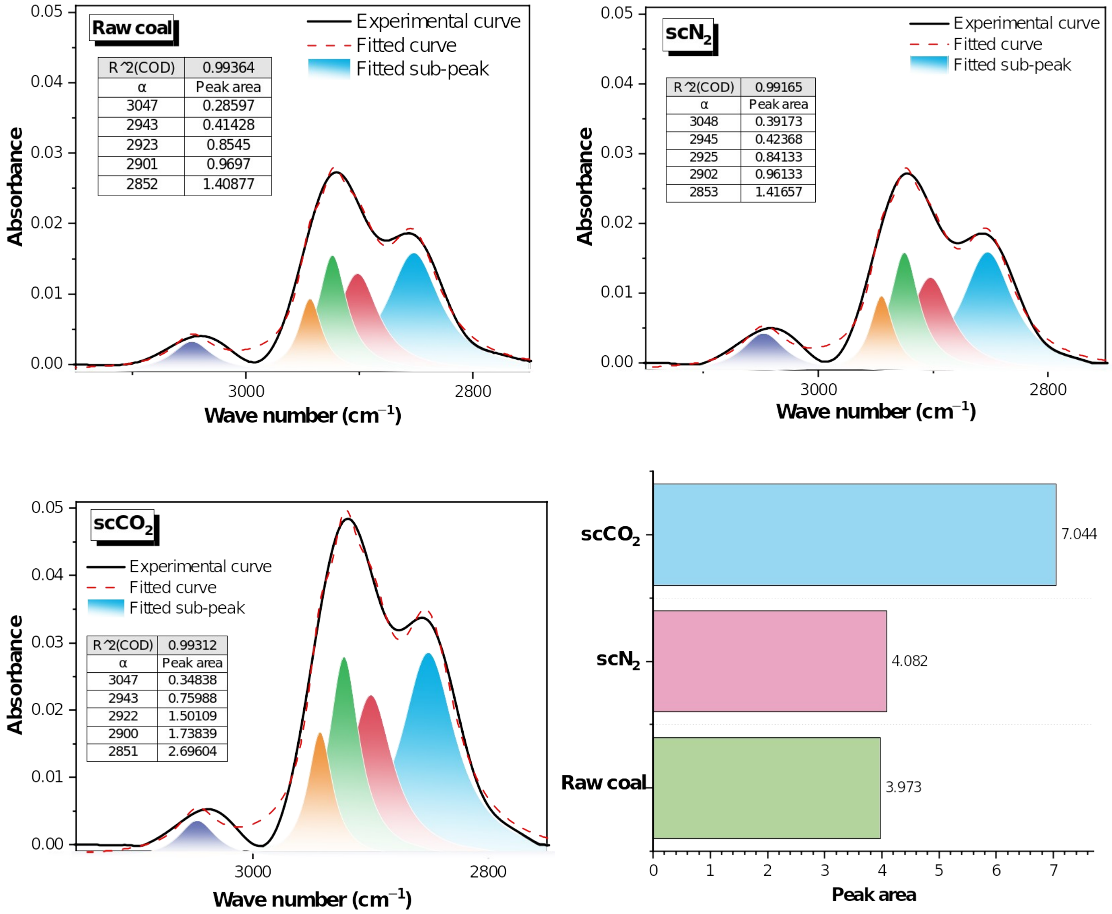
R^2(COD)	0.98757
α	Peak area
3899	0.0058
3845	0.01748
3778	0.01876
3688	0.01331
3629	0.03772
3530	0.03185

Figure 13 Curve-fitting of FTIR spectra in the range of 3700–3200 cm^{-1}. α in the tables represent peak wave number, cm^{-1}. Peak areas from the different conditions are compared in the lower right bar graph.

(2) Aliphatic hydrocarbons

In **Figure 14**, the absorption peaks in the range of 3000–2800 cm^{-1} were mainly assigned to asymmetric vibrations of $-CH_2$ and $-CH_3$, and symmetric vibrations of $-CH_2$ and $-CH_3$. The peak positions of the above functional groups are located around 2943 cm^{-1}, 2923 cm^{-1}, 2901 cm^{-1} and 2852 cm^{-1}, respectively.

The integral areas of sub-peaks of aliphatic hydrocarbons for coal with H_2O treated by $scCO_2$, scN_2 and raw coal were 7.04, 4.08, 3.97, respectively. The increase of aliphatic structure results from the alkylation of hydrocarbons under acidic conditions and implies an increase of the C atom ratio (Ni et al., 2019; Zhang et al., 2023). For $scCO_2$-H_2O treatment, the peak areas of the sub-peaks corresponding to $–CH_3$ and $–CH_2$ increased from 1.38 and 2.27 to 2.50 and 4.20, with $–CH_2$ having greater relative increase. A previous study (Guanhua et al., 2019) reported that wettability is positively correlated with the percentage area of $–CH_3$ and negatively correlated with $–CH_2$. This suggests that carbon content increased after the chemical reactions, and that increases in surface coverage with aliphatic hydrocarbons are detrimental to water-wetting.



Raw coal

R^2(COD)	0.99364
α	Peak area
3047	0.28597
2943	0.41428
2923	0.8545
2901	0.9697
2852	1.40877

scN_2

R^2(COD)	0.99165
α	Peak area
3048	0.39173
2945	0.42368
2925	0.84133
2902	0.96133
2853	1.41657

$scCO_2$

R^2(COD)	0.99312
α	Peak area
3047	0.34838
2943	0.75988
2922	1.50109
2900	1.73839
2851	2.69604

Figure 14 Curve-fitting of FTIR spectra in the range of 3000–2800 cm^{-1}. α in the tables represent peak wave number, cm^{-1}. Peak areas from the different conditions are compared in the lower right bar graph.

(3) Oxygen-containing functional groups

As shown in **Figure 15**, the absorption peaks of oxygen-containing functional groups were mainly in the range of 1800-1000 cm^{-1}. The functional groups were assigned to COOH, aromatic nucleus C=C, symmetric $–CH_3$, C–O, C–O–C, which located near 1705 cm^{-1}, 1595 cm^{-1}, 1362 cm^{-1}, 1206 cm^{-1}, and 1068 cm^{-1}, respectively.

The integral areas of the sub-peaks of oxygen-containing functional groups for raw coal, coal with H_2O treated by scN_2, and coal with H_2O treated by sc CO_2 were 38.28, 34.52, and 20.33, respectively. The decrease of oxygen-containing functional groups after $scCO_2$ treatment reflects their shedding or dissociation on the surface (Boehm, 1989). Oxygen-containing functional groups, including many polar components (Crawford et al., 1994), especially carboxyl groups, enhance interaction forces with polar molecules such as H_2O and are much stronger than the intermolecular forces (induced force and dispersion force) between CO_2 and oxygen-containing functional groups (Siemons et al., 2006). Therefore, it is difficult for CO_2 to displace H_2O molecules adsorbed directly on oxygen-containing functional groups at room-temperature and ambient-pressure (Gensterblum et al., 2014). Wu et al. similarly reported that reduction of oxygen-containing functional groups leads to weaker water-wetting as reflected in the shrinkage of precursor films and lower surface free energy (Wu et al., 2017). Shedding of polar oxygen-containing functional groups (especially carboxyl groups) after reactions with $scCO_2$ significantly weakened water-wetting.

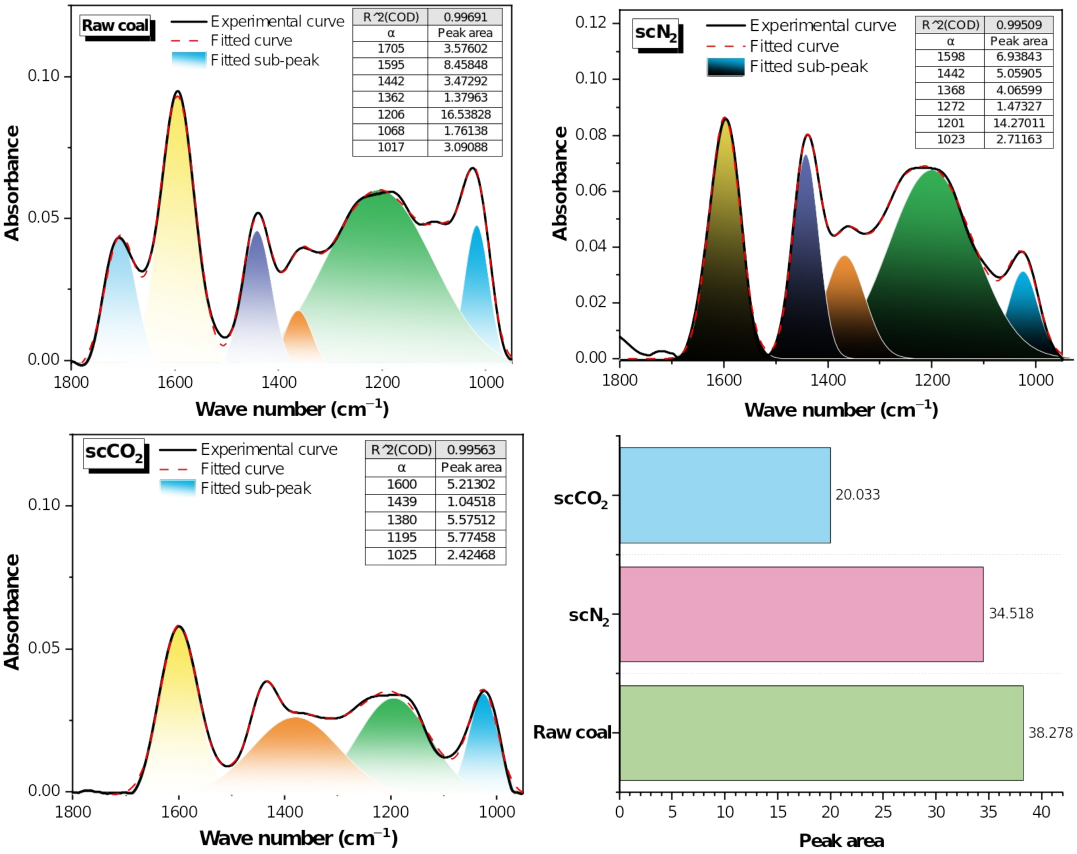
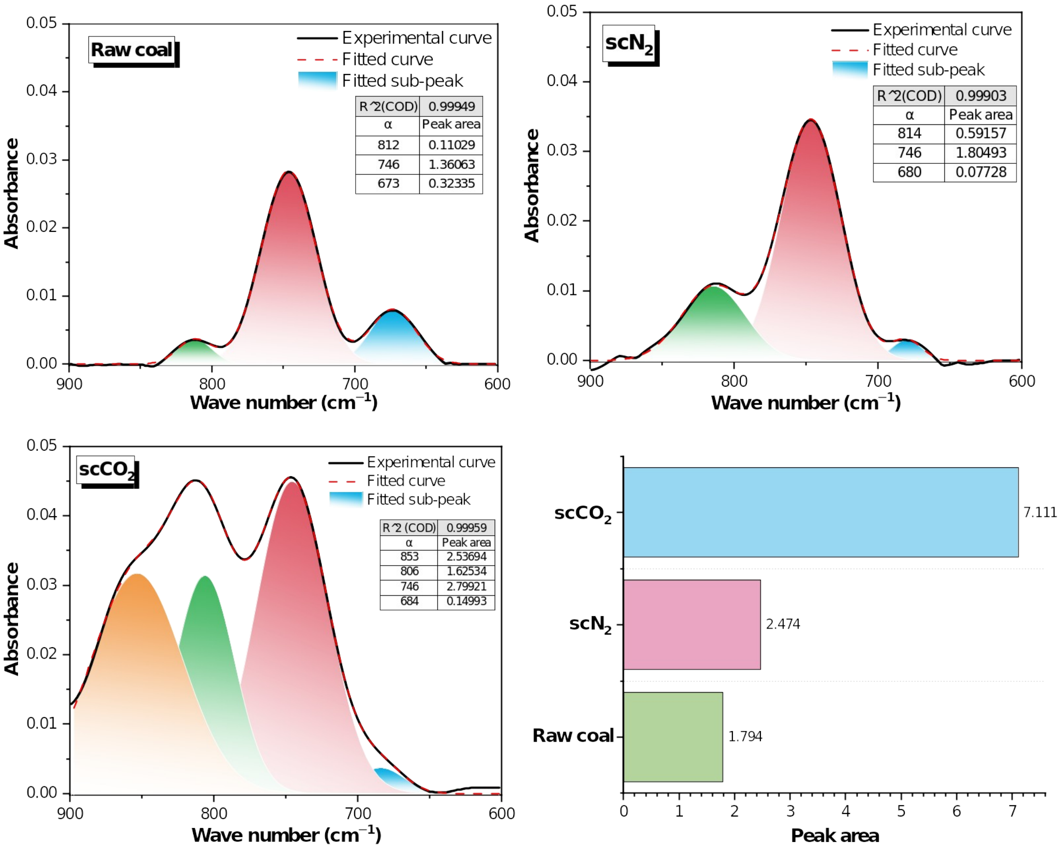


Figure 15 Curve-fitting of FTIR spectra in the range of 1800–1000 cm^{-1}. α in the tables represent peak wave number, cm^{-1}. Peak areas from the different conditions are compared in the lower right bar graph.

(4) Aromatic hydrocarbons

The adsorption peaks of waveband 900–600 cm^{-1} in **Figure 16** mainly were assigned to the bending vibrations of substituted benzene rings. Compared with aliphatic hydrocarbons, most of aromatic hydrocarbons are also insoluble in water, but the aromatic system is more stable.

The integral areas of the sub-peaks of aromatic hydrocarbons for raw coal, coal treated by scN_2 and by $scCO_2$ were 1.79, 2.47, and 7.11, respectively. After $scCO_2$ treatment, the peak intensities and peak areas of two sub-peaks near 853 cm^{-1}, 806 cm^{-1} increased significantly, which was attributed to the increase of aromatic structure content (Wang et al., 2023) (main contribution), CO_3^{2-} ions, and silica (Fatah et al., 2021b; Reig et al., 2002) .



R^2(COD)	0.99949
α	Peak area
812	0.11029
746	1.36063
673	0.32335

R^2(COD)	0.99903
α	Peak area
814	0.59157
746	1.80493
680	0.07728

R^2 (COD)	0.99959
α	Peak area
853	2.53694
806	1.62534
746	2.79921
684	0.14993

Figure 16 Curve-fitting of FTIR spectra in the range of 900–700 cm^{-1}. α in the tables represent peak wave number, cm^{-1}. Peak areas from the different conditions are compared in the lower right bar graph.

Infrared structural parameters used to characterize chemical structure are defined and reported in **Table 3**. We obtain the following conclusions:

1. Aromaticity (I) represents the abundance of aromatic hydrocarbons relative to aliphatic hydrocarbons. The increase of aromaticity implies the gradual decrease of coal defects and disorder.

2. CH_2/CH_3 represents the length of aliphatic chain and branching degree. The increase of CH_2/CH_3 indicate more aliphatic chain and less branched chains.

3. The degree of aromatic ring condensation (DOC) represents the ratio of aromatic C atoms to aromatic clusters and aromatic ring condensation. The increase of I, CH_2/CH_3, and DOC after $scCO_2$ treatment indicates more stable structure and elevated coal rank. Graphitization and hydrophobicity are eventually enhanced, as will be discussed

in 4.3 section.

Table 3 Infrared structure parameters.

Structure parameter	Formula	Experimental group		
		$scCO_2$	scN_2	Raw coal
Aromaticity	$I = \frac{A\square_{900\sim700}}{A_{3000\sim2800}}$	1.279	0.775	0.563
Degree of aromatic ring condensation	$DOC = \frac{A_{CH_2} + A_{CH_3}}{A_{C=C}} = \frac{A\square_{900\sim700}}{A_{1605\ 1595}}$	1.368	0.356	0.212
Length of aliphatic hydrocarbon chain	$A(CH_2)/A(CH_3) = \frac{A_{2920+2850}}{A_{2950+2870}}$	1.68	1.630	1.637

The overall impact of different treatments on surface chemistry is quantified by the average relative change of the absorption peak area ($\Delta^{'}A$), given by

$$\Delta^{'}A = \frac{1}{4}\sum_{i=1}^{4} \frac{\left|A\square_{(scN\square_2)i} - A\square_{(raw\,coal)i}\right|}{A\square_{(raw\,coal)i}} \tag{6}$$

From this metric, changes in functional group content from scN_2-H_2O treatment were small relative to the original raw coal, $reflected \in a\Delta^{'}A$ that is only 0.15 times that for the $scCO_2$-H_2O treatment. Such minor changes in surface chemistry imparted by exposure to scN_2, are consistent with small changes in measured contact angles. After $scCO_2$-H_2O treatment, the density of hydrophilic functional groups (hydroxyl and other polar oxygen-containing functional groups (Zhao et al., 2023)) decreased, while the hydrophobic functional groups (aromatic and aliphatic hydrocarbons (Xu et al., 2017)) increased. This tendency towards hydrophobicity results from three aspects: (1) the shedding of polar oxygen-containing functional groups, (2) the reduction of hydrogen bonds, (3) elevated coal rank and the increased percentage of surface hydrocarbons. Fewer sites of polar oxygen-containing functional groups were available for H_2O directly adsorbing (dark color in **Figure 17** (b)). The intermolecular force (hydrogen bonds between H_2O) and long-distance attractions weakened so that H_2O in multilayer adsorption (light color) was displaced or washed away by CO_2. Coal surfaces with a higher percentage of hydrocarbons and a tendency to be graphitized are more hydrophobic and more capable of CO_2 adsorption.

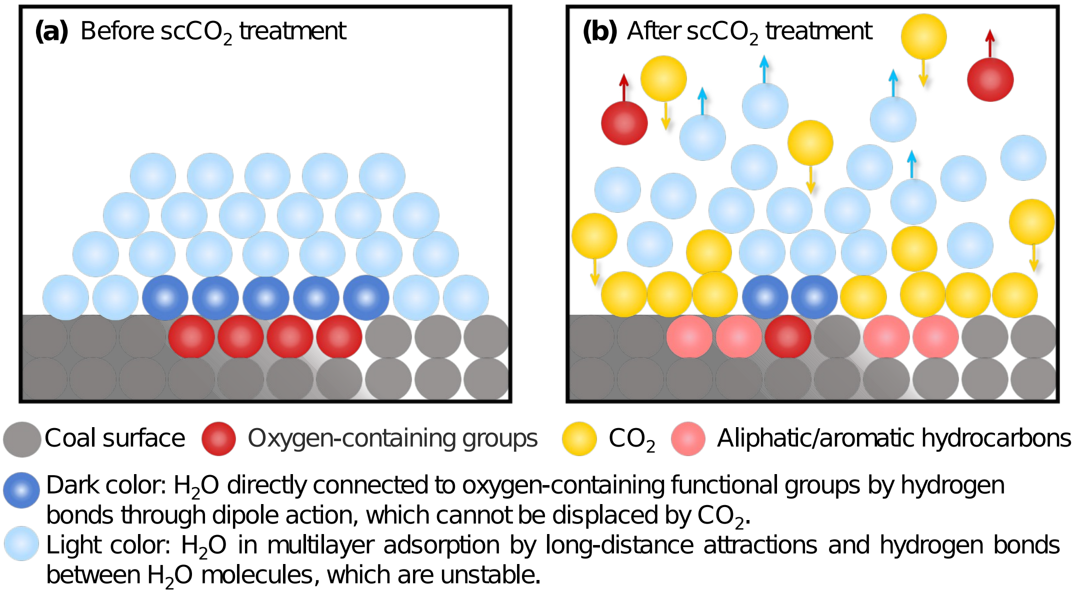


Figure 17 Schematic diagram of the effect of CO_2 adsorption and functional group alterations on wettability.

4.3 Coal crystallite structure

XRD patterns of coal generally have two diffraction peaks (002- and 100-peak) corresponding to diffraction angles (2θ) ~26° and 44°, respectively. The asymmetry of diffraction peak (raw curve in **Figure 18**) is caused by the γ-band related to saturated structures like aliphatic chains or aliphatic rings (Kamble et al., 2022). The 002-peak was distinct while the 100-peak was not, as shown in **Figure 18**, indicating that the main crystalline phase is carbon.

In general, the intensity of the diffraction peak decreased after $scCO_2$ treatment, indicating that mineral content decreased, especially calcite (club label near 2θ~30° in **Figure 18**), and only the diffraction peak of quartz (heart label) was still clearly present. As shown in **Figure 18**, residual analysis showed that conventional residuals at the peak position of calcite deviated clearly from mode-fitting values of cumulative curve. The diffraction peak of calcite was the reason for coefficient of determination $R^2<0.90$ in raw coal and scN_2 treatment. A previous study eliminated this strong peak in coal by acid leaching (Yan et al., 2020), causing the decomposition of calcite in carbonic acid as described by Eqs. (2).

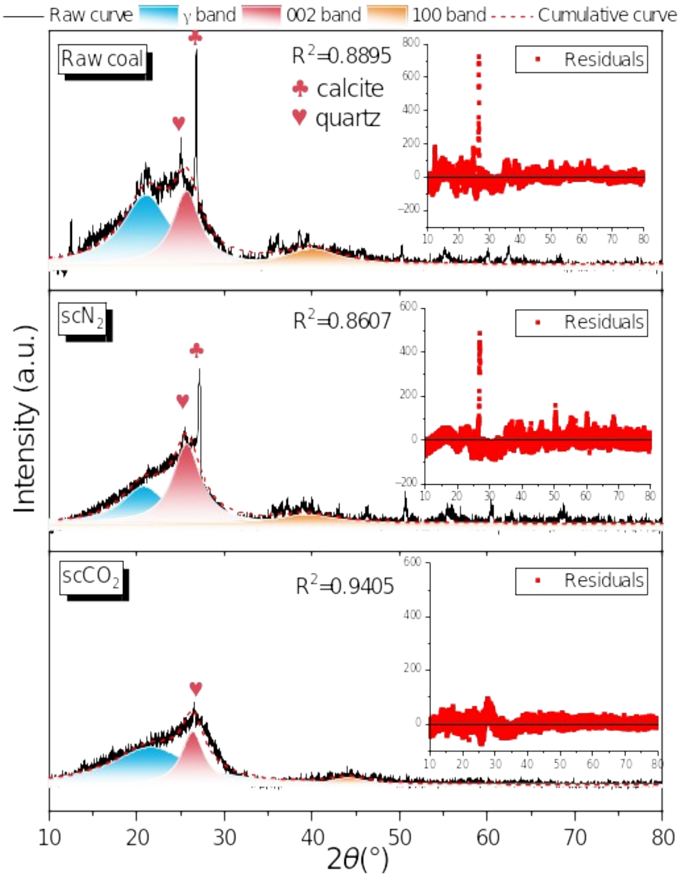


Figure 18 Curve-fitting of XRD patterns and residual analysis. The mineral labeling was accomplished through comparisons with standard cards in Jade and with previous work (Tian et al., 2017; Yan et al., 2020).

Crystallite structure parameters in **Table 4** were calculated with the Bragg's and Scherrer's formulae (7)–(11) (Matlala et al., 2021): aromatic interlayer spacing d_{002}, crystallite diameter L_a, crystallite height L_c, the number of aromatic stacking layers N, and coalification degree D. Full width at half maximums (FWHM) and peak mean centers of 002- and 100-peak used to calculate crystallite parameters were obtained from the fitting results shown in **Table A.2**.

The d_{002} for raw coal, scN_2 treatment, and $scCO_2$ treatment were 3.46 Å, 3.46 Å, 3.37 Å, respectively, and the reduction of interlayer spacing implied closer arrangement of aromatic layer structure. For $scCO_2$ treatment, the diffraction angle of 002-peak was 26.4° and close to that of pure graphite (26.6°). L_a, L_c, and N both increased, indicating the degree of molecular polymerization and the size of carbon crystalline developed (Sonibare et al., 2010). The D for raw coal, scN_2 treatment, and $scCO_2$ treatment were 82.3%, 82.6%, and 97.1%, respectively. From the XRD patten of the $scCO_2$ treated coal, we find that inorganic mineral abundance reduced, and carbon crystallites tended to graphite-like structure: the crystallite growth and the higher degree of long-range ordering in aromatic carbon (Zhang et al., 2021). These changes to crystallite structure are usually detrimental for water-wetting because of the higher carbon content and the lower negative surface charge after structure development (Fuerstenau et al., 1988). Moreover, crystallite development usually is associated with elevated coal rank, which is positively correlated with contact angle (Shojai Kaveh et al., 2012; Yan et al., 2015).

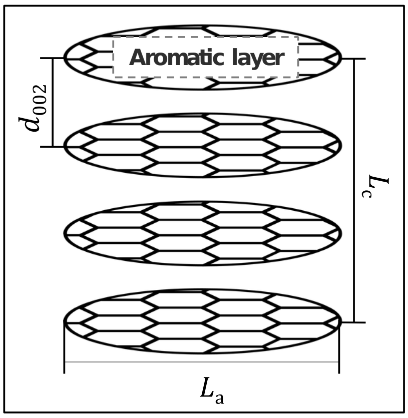
$$d_{002}=\frac{\lambda}{2\sin\theta_{002}} \tag{7}$$

$$L_a=\frac{K_1\lambda}{\beta_{(100)}\cos\theta_{(100)}} \tag{8}$$

$$L_c=\frac{K_2\lambda}{\beta_{(002)}\cos\theta_{(002)}} \tag{9}$$

$$N=\frac{L_c}{d_{002}}+1 \tag{10}$$

$$D=\frac{d❑_{CE}-d_{002}}{d❑_{CE}-d❑_{GR}}\times 100\% \tag{11}$$



where λ is the X-ray wavelength, the copper target is taken as 1.54056 Å; $\theta_{(002)}$, $\theta_{(100)}$ are the Bragg angles of the 002 and 100 diffraction peaks, respectively, (°); $\beta_{(002)}$, $\beta_{(100)}$ are the half-height widths of the 002 and 100 diffraction peaks, respectively, (rad); K_1, K_2 are Debye-Scherrer constants and crystallite shape factors. K_1, K_2 are taken as 1.84, 0.94, respectively. $d❑_{CE}$ and $d❑_{GR}$ are cellulose of $d_{002}=$¿3.975 Å and graphite of $d_{002}=$¿3.354 Å, respectively.

Table 4 Crystallite structure parameters.

Coal sample	d_{002}**/ Å nm**	L_a**/ Å**	L_c**/ Å**	N	D/%
Raw coal	3.46	25.69	23.80	7.87	82.28%
N$_2$	3.46	21.93	20.84	7.02	82.61%
CO$_2$	3.37	37.64	26.16	8.76	97.08%

5 Implications

In this study, the interaction of CO_2-H_2O-coal systems were shown to change coal surfaces from water-wetting to intermediate-wetting. This determines the pore-scale configuration of fluids and fluid flow, thereby affecting reservoir-scale fluid dynamics.

After CO_2 treatment, hvBb coal in the situ reservoir condition (P=120 bar, T=45°C) is favorable for CO_2-ECBM projects. In this case, reduced capillary forces favor CO_2 injection and percolation rate in coal seams (Sakurovs and Lavrencic, 2011; Arif et al., 2016b), resulting in a wider and more homogeneous distribution of CO_2. CO_2 displacement efficiency is evaluated by capillary number N_{ca}, where larger contact angles makes N_{ca} larger, i.e., water or methane is more easily displaced (Shojai Kaveh et al., 2011).

$$N_{ca}=\frac{\mu \times v}{\gamma_{lg} \times cos\theta} \tag{12}$$

The wetting phase transition is also favorable for overcoming the water blocking effect (water as the wetting phase blocks the methane in the micropores) that affects hydraulic fracturing (Li et al., 2022). CO_2, as the wetting phase, can enter the micropores and displace methane due to its stronger adsorption capacity (Pini et al., 2010).

However, this alteration also imparts a detrimental impact on CO_2 sequestration because storage capacity under caprock is limited by the balance between capillary force and buoyancy. This balance limits the permanently immobilized CO_2 storage height h (Iglauer, 2018)

$$\begin{cases} P_c \wedge \text{¿} \frac{2\gamma cos\theta}{r} \\ P_b = \Delta\rho g h \end{cases} \Longrightarrow h=\frac{2\gamma cos\theta}{\Delta\rho g r} \tag{13}$$

Increasing contact angles indicate the decrease in storage capacity and containment security. The advancing and receding contact angles measured in this study reflect fluid migration processes such as displacement and flowback, and can be utilized to predict and improve field practices, including nanoparticles, surfactants, and polymers used to modify wettability (Ali et al., 2023).

6 Conclusions

We measured time-dependent dynamic and static contact angles (CA) on coal surfaces exposed to CO_2/N_2- H_2O using the captive bubble method, with the nonaqueous phase in gaseous and supercritical states. We characterized physicochemical properties by FTIR, XRD, and SEM in order to identify the mechanisms responsible for weakening water-wetting after $scCO_2$ treatment. The main conclusions are as follows.

(1) The contact angles (CAs) for gas and supercritical N_2 treatment only changed slightly. For gaseous CO_2 treatment, the dynamic CA also varied slightly. For $scCO_2$ treatment, both the static and dynamic CAs increased significantly, and the average θ_{adv} changed from water-wet (27° for scN_2 treatment) to intermediate-wet (92°).

(2) The chemical reactions of minerals resulted in inhomogeneous and rougher surfaces with corrosion pores, connecting partially isolated pores, fracture extension, and edge warping, finally generating greater contact angle hysteresis; all which favor

CO_2-wetting.

(3) The abundance of hydrophilic functional groups decreased while that of hydrophobic functional groups increased following $scCO_2$ treatment. The unfavorable water-wet changes were reflected in four aspects: the shedding of polar oxygen-containing functional groups, the reduction of hydrogen bonds, elevated coal rank, and increased percentage of hydrocarbons.

(4) $scCO_2$ treatment depleted most of the inorganic mineral components (most notably calcite). The molecular polymerization of carbon was higher and crystallites developed toward graphite-like growth and elevated coal rank. These changes in crystallite structure are not favorable for water-wetting due to the higher carbon content and lower surface charge.

CRediT authorship contribution statement

Ke Li: Investigation, Writing–original draft, Formal analysis, Visualization. **Chuanjie Zhu:** Writing–review & editing, Methodology, Funding acquisition, Supervision. **Jiamin Wan:** Writing–review & editing, Conceptualization, Supervision, Resources. **Tetsu K. Tokunaga:** Writing–review & editing, Supervision. **Na Liu:** Investigation. **Cong Ma:** Investigation. **Baiquan Lin:** 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.

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Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Table A. 1 Mineral compositions of raw coal

Category	Common Minerals	Chemical formula
Silicate mineral (clay)	Kaolinite	$Al_4(Si_4O_{10})(OH)_8$
	Illite (hydromica)	$K_{1-1.5}Al_4(Si_{7-6.5}Al_{1-1.5}O_{20})(OH)_4$
	Chlorite	$(Mg,Fe,Al)_{12}[(Si,Al)_8O_{20}](OH)_{16}$
	Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$
	Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
Carbonate mineral	Calcite	$CaCO_3$
	Siderite	$FeCO_3$
	Dolomite	$CaMg(CO_3)_2$
Oxide mineral	Quartz (chalcedony)	SiO_2
	Hematite	Fe_2O_3
Sulfide mineral	Pyrite, marcasite	FeS_2

Table A.2 Fitting peak information in XRD for calculating semi-quantitative structural parameters

Peak type	Group	FWHM			2 (weighted average center)		
		γ-band	002-band	100-band	γ-band	002--band	100-band
Lorentz	Raw coal	7.06641	3.38373	6.7259	21.07246	25.6866	40.01169
Lorentz	scN_2	5.92757	3.86474	7.86542	20.81895	25.7018	39.43583
Lorentz	$scCO_2$	10.75628	3.08301	4.65443	21.58649	26.39881	44.11167

Table A.3 Dynamic contact angle under gaseous N_2 (P=20bar, T=25°C)

Time (hours)	Left-Adv.	Right-Adv.	θ_{adv}	Left-Rec.	Right-Rec.	θ_{rec}
0	28	28	28	24	23	23.5
24	33	31	32	23	22	22.5
48	29	30	29.5	25	19	22
72	31	27	29	26	19	22.5

96	30	29	29.5	23	22	22.5

Table A.4 Dynamic contact angle under scN_2 (P=120bar, T=45°C)

Time (hours)	Left-Adv.	Right-Adv.	θ_{adv}	Left-Rec.	Right-Rec.	θ_{rec}
0	29	28	28.5	21	21	21
24	29	28	28.5	22	21	21.5
48	26	23	24.5	20	17	18.5
72	28	25	26.5	22	20	21
96	27	26	26.5	21	21	21

Table A.5 Time-dependent static CAs under N_2.

Time	Average static contact angle (°)	
hours	gaseous N_2	scN_2
0	24	23
24	25	22
48	24	23
72	23	24
96	23	23

Table A.6 Dynamic contact angle under gaseous CO2 (P=20bar, T=25°C)

Time (hours)	Left-Adv.	Right-Adv.	θ_{adv}	Left-Rec.	Right-Rec.	θ_{rec}
0	40.3	51.0	45.7	19.9	18.0	19.0
24	32.4	35.8	34.1	23.2	19.0	21.1
48	36.8	42.0	39.4	24.2	24.6	24.4
72	31.4	38.6	35.0	24.0	20.6	22.3
96	37.3	38.5	37.9	21.8	19.4	20.6

Table A.7 Dynamic contact angle under $scCO_2$ (P=120bar, T=45°C)

Time (hours)	Left-Adv.	Right-Adv.	θ_{adv}	Left-Rec.	Right-Rec.	θ_{rec}
0	93.4	89.6	91.5	36.4	33.2	34.8
24	91.0	85.8	88.4	33.4	30.8	32.1
48	95.0	89.6	92.3	46.0	42.0	44.0
72	94.0	92.5	93.3	42.5	45.7	44.1
96	96.0	93.0	94.5	52.2	47.0	49.6

Table A.8 Time-dependent static CAs under CO_2.

Time(hours)	Static contact angle	
	gaseous CO2	$scCO_2$
0	22.5	35.0
24	22.0	44.2

48	25.8	52.4
72	24.4	53.4
96	23.9	55.7