

Article

Supercritical CO₂ Exposure-Induced Surface Property, Pore Structure, and Adsorption Capacity Alterations in Various Rank Coals

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Abstract: Carbon dioxide (CO₂) has been used to replace coal seam gas for recovery enhancement and carbon sequestration. To better understand the alternations of coal seam in response to CO₂ sequestration, the properties of four different coals before and after supercritical CO₂ (ScCO₂) exposure at 40 °C and 16 MPa were analyzed with Fourier Transform infrared spectroscopy (FTIR), low-pressure nitrogen, and CO₂ adsorption methods. Further, high-pressure CO₂ adsorption isotherms were performed at 40 °C using a gravimetric method. The results indicate that the density of functional groups and mineral matters on coal surface decreased after ScCO₂ exposure, especially for low-rank coal. With ScCO₂ exposure, only minimal changes in pore shape were observed for various rank coals. However, the micropore specific surface area (SSA) and pore volume increased while the values for mesopore decreased as determined by low-pressure N₂ and CO₂ adsorption. The combined effects of surface property and pore structure alterations lead to a higher CO₂ adsorption capacity at lower pressures but lower CO₂ adsorption capacity at higher pressures. Langmuir model fitting shows a decreasing trend in monolayer capacity after ScCO₂ exposure, indicating an elimination of the adsorption sites. The results provide new insights for the long-term safety for the evaluation of CO₂-enhanced coal seam gas recovery.

Keywords: super-critical CO₂; coal rank; surface property; pore structure; adsorption

1. Introduction

Recently, concerns about increasing carbon dioxide (CO_2) concentration in the atmosphere have driven research into the technical reduction of the emission of CO_2 from fossil fuel use [1]. Carbon capture and storage (CCS) is an effective approach for CO_2 mitigation currently under consideration [2,3]. Deep, un-minable coal seams have been targeted as safer sites for CO_2 sequestration because the sequestrated CO_2 is predominantly stored as a relatively stable adsorption phase in coal seams. Meanwhile, the replacement of coal seam gas (CSG) offsets some proportion of sequestration costs [4–6]. Accordingly, an understanding of the physical and chemical alterations of coal reservoirs in response to CO_2 sequestration would offer a scientific foundation on which to base long-term storage predictions.



Recently, several studies have investigated the chemical and structural properties of various rank coals [7–10]. These studies have demonstrated that coal mass is an organic-rich porous rock, consisting of micropores (<2 nm in diameter) and mesopores (2–50 nm in diameter) in coal matrix and cleats (>50 nm in diameter). The structural properties of coal vary with the degree of maturity as determined by reflectance or volatile matter [11]. In the CO₂-enhanced coal bed methane recovery (CO₂-ECBM) process, CO₂ fluids first flow into the cleat system of coal mass and then slowly diffuse into mesopores and micropores, CO₂ can displace the pre-adsorbed CSG through the competitive adsorption mechanism, thus achieving CO₂ storage and CSG enhancements [12].

The swelling effect of coal matrix induced by CO_2 adsorption has been reported extensively [13–16]. As reviewed by Perera et al. [17], the swelling of the coal matrix is accompanied by a series of irreversible effects on coal seam, including the variation of coal seam permeability and mechanical properties. The matrix swelling effect is closely related to coal rank, where higher-ranked coal exhibits a lower matrix swelling rate [18]. Normally, the potential coal seams for CO_2 sequestration are at depths of 800–1000 m, where temperature and pressure are beyond the critical point of CO_2 ($T_c = 31.8 \ ^{\circ}C$, $P_c = 7.38 \ ^{\circ}MPa$) and CO_2 exists in its supercritical phase. Supercritical CO_2 (ScCO₂) exhibits liquid-like density and dissolution power as well as gas-like viscosity and transport behavior [19]. Laboratory experiments have demonstrated that ScCO₂ adsorption causes a significantly higher coal matrix swelling effect in comparison with subcritical CO_2 adsorption due to the higher uptake capacity of ScCO₂ [6,20]. Further, Hol et al. [21] revealed that the adsorption-induced heterogeneous swelling at the maceral scale, accompanied by differential accessibility of the coal microstructure, can form microfractures in the coal mass. In this respect, the sequestrated CO_2 may alter the pore morphology of the coal mass during long-term storage.

In addition to the adsorption-induced coal matrix swelling effect, CO₂ molecules can dissolve into the coal matrix, especially when CO₂ exists in a supercritical state [22,23]. According to Goodman et al. [24], CO₂ is a more chemically potential adsorbate than CSG and can act as plasticizer of coal mass, leading to a potential structural rearrangement that affects the molecular structure or intermolecular bonding of coal matrix. Moreover, ScCO₂ can act as a solvent capable of extracting organic hydrocarbons from the coal matrix as demonstrated by Kolak and Burruss [25]. Their experiments demonstrated that the extracted amount and type of hydrocarbons varied for different rank coals, with the highest hydrocarbon concentrations mobilized from high volatile bituminous coal.

In consideration of the effects of the fluid-solid interaction between $ScCO_2$ and coal matrix, it is essential to evaluate the chemical and structural alterations in coal with $ScCO_2$ exposure. The alterations in coal properties may further change the flow behavior and adsorption capacities of CO_2 on the coal mass, thus influencing the substantial CO_2 injection rate and CSG recovery efficiency. Previous studies only considered the effects of $ScCO_2$ on the chemical and structural properties of the coal mass. Systematic knowledge of the adsorption capacity alteration of various rank coals with $ScCO_2$ exposure is still needed to better estimate the feasibility of CO_2 sequestration in coal seams.

The objective of this study is to investigate the variation of chemical and structural properties as well as the corresponding alteration of the adsorption capacity in response to ScCO₂ exposure for various rank coals. To address this issue, Fourier transform infrared spectroscopy (FTIR) analysis, low-pressure N₂ and CO₂ sorption method, and high-pressure CO₂ adsorption experiments were conducted on four Chinese coals of different rank.

2. Materials and Methods

2.1. Sample Collection and Preparation

Four coal samples collected from coal mines in China were used in this study: lignite from No. 1–2 coal seam in Daliuta coal mine, Shendong coal field (DL coal); middle volatile bituminous coal from No. 2 coal seam in Zhaolou coal mine, Heze coalfield (ZL coal); low volatile bituminous coal from No. C-9 coal seam in Guiyuan coal mine, Guizhou coalfield (GY coal); anthracite from No. 6 coal seam in

Datong coal mine, Sichuan coalfield (DT coal). The information of the sampling coal mines is shown in Figure 1.



Figure 1. The information of the sampling coal mines: (a) location, and (b-e) stratigraphic column.

Coal blocks were first drilled from freshly exposed mining faces and then immediately sealed in a plastic bag and transported to the laboratory. To accelerate the coal– $ScCO_2$ interaction, all the coal lumps were crushed and sieved to particles of 18–20 mesh. Proximate and ultimate analyzes were carried out to characterize coal samples. The analysis results are presented in Table 1.

Sample	Romax (%)	Proximate Analysis (wt %)				Ultimate Analysis (wt % daf)			
1	U max (V)	C_{fix}	V_{daf}	A _{ad}	M	С	H	N	0
DL coal	0.42	53.55	36.96	19.42	2.46	72.71	4.95	1.19	20.50
ZL coal	0.81	65.10	28.71	16.24	1.50	82.54	4.57	1.08	11.03
GY coal	1.14	78.34	6.14	10.52	2.08	86.92	4.01	1.20	6.03
DT coal	1.86	73.85	12.81	13.34	1.96	90.11	3.79	0.96	2.05

Table 1. Proximate and ultimate analyzes of the coal samples.

Notes: *C_{fix}*, fixed carbon; *V_{daf}*, volatile matters; *A_{ad}*, ash; *M*, moisture.

2.2. Exposure of Coal to ScCO₂

In this study, the raw coal samples were firstly saturated to $ScCO_2$ and then further tests were conducted to compare coal properties alteration before and after $ScCO_2$ exposure. A specific high-pressure sealed vessel was fabricated and used to saturate the coal samples with $ScCO_2$ as schematically shown in Figure 2. The heart of this apparatus are pressure cells, an ISCO (260D) syringe pump (Teledyne ISCO, Lincoln, NE, USA) and the data system. The sample was first inserted into the pressure cell with a temperature-controlled thermostatic water bath with an accuracy of \pm 0.1 °C. Then, CO₂ was injected from the gas cylinder into the sample cell by the ISCO syringe pump. Prior to interaction, the system was degassed under vacuum at 60 °C for 12 h. The reaction pressure was set as 16 MPa, with a constant temperature value of 40 °C, simulating CO₂ injection into deep (~800 m) coal seams [17]. The exposure time was set at 30 days to ensure a sufficient coal–ScCO₂ interaction. After the saturation period, the sample cell was gradually de-pressurized by 0.1 MPa/min to avoid possible damage to the coal samples. The coal samples were then covered with plastic wrap to avoid any possible changes to the saturation state. All the tests were repeated three times to increase the confidence level and reliability. The average data of three tests were used in this study.



Figure 2. Schematic diagram of coal–ScCO₂ interaction system.

2.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The surface functional groups of both the raw and ScCO₂-treated coal samples were determined using a FTIR Nicelet 6700 (Thermo Fisher Scientific, Waltham, MA, USA). The coal samples for FTIR analysis were prepared following the potassium bromide (KBr) pellet method. The coal powders (0.5–1 mg in weight) and the dried KBr were ground at a mass ratio of 1:160. The spectral was obtained in the 400 cm⁻¹ and 4000 cm⁻¹ wavenumber regions with a resolution of 4 cm⁻¹.

2.4. Low-Pressure N₂ and CO₂ Isotherm Measurements

Low-pressure gas adsorption measurements were conducted on an Accelerated Surface Area and Porosimeter System ASAP 2020M (Micrometrics Instruments Corporation, Norcross, GA, USA). Using standard adsorbates N₂ and CO₂, information about the mesopore and micropore structure of the coal samples was obtained. Before analysis with either N₂ or CO₂, the samples (weighing 1–2 g) were degassed under vacuum by heating at 105 °C for 12 h to remove water and other volatile matter. The adsorption-desorption isotherms of N₂ were measured at liquid nitrogen (–196.15 °C) under the relative pressure ranging from 0.005 to 0.99. The isotherms of CO₂ adsorption were performed at 0 °C under the relative pressure of 0.005–0.032.

At each pressure set point, the sorption equilibrium was established automatically when the system pressure remained stable for 30 s. The absolute pressure tolerance was set as 5 mmHg (6.66 mbar). After each test, the specific surface area (SSA), pore volume, and pore size distribution (PSD) of the coal samples were calculated based on multiple models.

2.5. High-Pressure CO₂ Isotherm Measurements

High-pressure CO_2 adsorption isotherms were performed using a gravimetric analyzer IGA (Hiden Isochema Limited, Warrington, UK). A detailed description of the IGA system and the general adsorption isotherm test procedure can be found in reference [26]. All isotherms were measured to a pressure of 1.8 MPa at 40 °C. Prior to tests, the samples were degassed at 105 °C under vacuum (<10⁻⁶ Pa) for 12 h to remove the water content from the samples. During the experiment, equilibrium was established when the rate of sample weight change was less than 1% or a time limit was reached. Then, the gas pressure was regulated to the next step. The buoyancy effect was corrected automatically in the measurement.

3. Results and Discussion

3.1. Effect of ScCO₂ Exposure on Coal Surface Property

The effect of $ScCO_2$ exposure on surface property of various rank coals was examined by FTIR spectroscopy, a technique well suited to study the surface functionalities. The FTIR spectra for the raw and $ScCO_2$ -treated coal samples are shown in Figure 3. As presented in Figure 3, the FTIR spectra of

the coal samples were typical of complex, heterogeneous organic materials containing multiple type of surface functional groups. With ScCO₂ exposure, both the -OH groups (at a wave number of around 3450 cm^{-1}) and the amide carbonyl groups (at a wave number of around 1620 cm^{-1}) show an obvious decrease for DL coal, ZL coal, and GY coal, with only a slight decrease for DT coal. The prominent bands at the wave number around 1000 cm^{-1} possibly contributed to mineral matter and clay, which show an obvious decrease for all the coals after ScCO₂ exposure, indicating an elimination of mineral matter and clay. The bands ranging 900–400 cm⁻¹ show an obvious decrease for DL coal and DT coal after ScCO₂ exposure, which is attributed to the Si-O and Si-O-Al bands.



Figure 3. Fourier transform infrared spectroscopy (FTIR) spectra for the raw and ScCO₂-treated coal samples: (**a**) DL coal; (**b**) ZL coal; (**c**) GY coal; (**d**) DT coal.

In a comparison of the spectra of the raw and ScCO₂-treated coal samples, obvious variations were found in functional group distribution, especially for the low-rank coal. According to Wang et al. [27], the decrease in surface functional group density may be attributable to the extracting effect or reactivity of ScCO₂ fluid. The decrease of -OH groups may be related to the dissolution of ScCO₂ to the inherent moisture in the coal samples; however, the elimination of the amide carbonyl groups may be related to the extraction of the organic volatile corresponds from coal with ScCO₂ exposure, as demonstrated by Li et al. [28]. In addition, a decrease in the distribution of mineral matter content in the coal samples was observed after ScCO₂ exposure. However, Mastalerz et al. [29] detected no change in the functional groups of two different coal samples after saturation with CO₂. This is because the saturation conditions they conducted were at 20 °C and 4.14 MPa where CO₂ was in a sub-critical state in which it cannot extract corresponds from coal matrix. The loss of the organic and inorganic corresponds in the coal matrix with ScCO₂ exposure may influence its adsorption capacity for CO₂, which will be discussed later in this study.

3.2. Effect of ScCO₂ Exposure on Coal Pore Structure

3.2.1. Low-Pressure N2 and CO2 Sorption Isotherms

The adsorption-desorption isotherms of N₂ on the raw and ScCO₂-treated coal samples at -196 °C are shown in Figure 4. All the isotherms correspond to the type IV isotherm of IUPAC classification [30]. This type of isotherm is considered to be associated with the distribution of mesopores in solids [31]. Distinct adsorption-desorption hysteresis loop is observed in each isotherm at a high relative pressure (>0.45). The presence of the hysteresis loop suggests that capillary condensation occurred within the mesopores. The shape of the hysteresis loop is a reflection of pore morphology within the coal matrix [32]. As shown in Figure 4, there is only a slight difference in the shape of the hysteresis loop in the isotherms between the raw and ScCO₂-treated coal samples. It can be deduced that interaction with ScCO₂ has a minimal influence on pore shape in various rank coals. This is consistent with previous studies [33,34].

Figure 4 also shows that the adsorbed amount of N_2 on the ScCO₂-treated coal samples is lower than that on the raw samples, suggesting that the adsorption capacity of N_2 on various rank coals uniformly decreased after ScCO₂ exposure. At relative pressure less than 0.2, there is no distinct difference in N_2 adsorption capacity between the raw and ScCO₂-treated coal samples. With the elevated relative pressure, the adsorption amount for the raw coal samples increases more rapidly than the ScCO₂-treated coal samples. This implies that exposure to ScCO₂ mainly influences the multilayer capacity of N_2 adsorption. In this respect, exposure to ScCO₂ may have a more distinct effect on the broader mesopores than on the narrow mesopores.



Figure 4. N₂ adsorption-desorption isotherms on the raw and ScCO₂-treated coal samples at –196 °C: (a) DL coal; (b) ZL coal; (c) GY coal; (d) DT coal.

The N₂ adsorption-desorption method can only provide mesopore information of the coal samples because N₂ molecules cannot penetrate the fine micropores and pore shrinkage of coal at the extremely low temperature of -196.15 °C. Low pressure CO₂ adsorption at 0 °C can overcome this drawback due to the shorter equilibrium time and disappearance of the pore shrinkage effect [35].

Figure 5 shows the adsorption isotherms of CO₂ on the raw and ScCO₂-treated coal samples at 0 °C under a low relative pressure (≤ 0.033). A comparison of Figures 4 and 5 reveals that, for various rank coals, the adsorption capacity of CO₂ is larger than N₂ at the same relative pressure due to the accessibility of CO₂ molecules to the narrow micropores of coal matrix in comparison with N₂ molecules. Figure 5 shows that the low-pressure adsorption capacity of CO₂ on the ScCO₂-treated coal samples is higher than that on the raw coal samples. This observation suggests an increase of accessibility in the micropores after ScCO₂ exposure, potentially attributable to the micro-fracturing of the coal matrix with ScCO₂ exposure, as demonstrated by Hol et al. [21].



Figure 5. Low-pressure CO₂ adsorption isotherms on the raw and ScCO₂-treated coal samples at 0 °C: (**a**) DL coal; (**b**) ZL coal; (**c**) GY coal; (**d**) DT coal.

3.2.2. Pore Properties Determined by Low-Pressure N2 and CO2 Sorption

The mesopore specific surface area (SSA) and total pore volume (V_t) of the coal samples with N₂ adsorbate were evaluated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, respectively. The SSA and micropore volume (V_{mic}) with CO₂ adsorbate were evaluated by Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (D-A) models [27]. These data can be calculated automatically by the analytical software in ASAP2020.

The estimated SSA and pore volume of the raw and ScCO₂-treated coal samples from N₂ and CO₂ sorption data are summarized in Table 2. The results show that, with ScCO₂ exposure, the mesopore SSA and V_t of the coal samples are slightly decreased, as seen in Figure 6. As shown in Table 2, reductions of about 0.366 to 0.065 m²/g of mesopore SSA and 9×10^{-3} to 2×10^{-3} cm³/g of V_t values can be observed after ScCO₂ exposure. These results indicate that the accessibility of mesopore in various rank coals decreased after ScCO₂ exposure. This may have been induced by the irreversible swelling effect of the coal matrix, which may block the pathways of gas molecules and reduce the pore volume [36]. With regard to the average pore width (*D*), the average pore diameter of GY coal reduced sharply after ScCO₂ exposure while the values for DL coal, ZL coal and NM coal increased

slightly. This may be due to the larger matrix swelling of GY coal by ScCO₂ exposure than the other coal samples.

Unlike mesopore, the values of micropore SSA and V_{mic} for the coal samples increased notably with ScCO₂ exposure, as seen in Figure 7. According to Table 2, the D-R SSA (S_{D-R}) and D-A SSA (S_{D-A}) determined by CO₂ adsorption exhibit a similar trend with a 15.8 to 137.0 m²/g and 19.3 to 44.2 m²/g increase for various rank coals, respectively. Simultaneously, increases of 0.005 to 0.014 cm³/g of V_{mic} values can be observed after ScCO₂ exposure. The increased amount of micropore SSA and V_{mic} in GY coal is the largest, followed by DT coal, DL coal, and ZL coal, respectively.

Table 2. Structural properties of the raw and $ScCO_2$ -treated coal samples determined by N_2 and CO_2 sorption.

Sample	State	N_2	Adsorption		CO ₂ Adsorption			
		$S_{\rm BET}/{\rm m}^2 \cdot {\rm g}^{-1}$	$V_{\rm t}/{\rm cm^3 \cdot g^{-1}}$	D/nm	$S_{\text{D-R}}/\text{m}^2 \cdot \text{g}^{-1}$	$S_{\text{D-A}}/\text{m}^2 \cdot \text{g}^{-1}$	$V_{\rm mic}/{\rm cm^3 \cdot g^{-1}}$	
DL coal	raw coal	1.498	0.0068	18.16	98.71	61.05	0.0216	
	ScCO ₂ -treated	1.132	0.0060	21.20	118.5	84.18	0.0327	
ZL coal	raw coal	0.744	0.0043	23.12	54.54	45.77	0.0219	
	ScCO ₂ -treated	0.611	0.0041	26.84	92.65	65.10	0.0268	
GY coal	raw coal	0.616	0.0028	18.19	222.4	160.9	0.0667	
	ScCO ₂ -treated	0.551	0.0019	13.79	359.4	205.1	0.0810	
DT coal	raw coal	0.586	0.0016	10.92	120.4	74.34	0.0264	
	ScCO ₂ -treated	0.387	0.0011	11.37	176.6	100.6	0.0353	



Figure 6. Mesopore specific surface area (SSA) and volume of the raw and ScCO₂-treated coal samples: (a) mesopore SSA; (b) mesopore volume.



Figure 7. D-R micropore SSA and volume of the raw and ScCO₂-treated coal samples: (**a**) micropore SSA; (**b**) micropore volume.

In combination with the N₂ and CO₂ adsorption results, the alterations of the pore structure in various rank coals were mainly controlled by two distinct mechanisms: (1) the extraction effect of ScCO₂ removes some volatile matters in the pore medium; (2) S_CCO_2 exposure induces irreversible swelling which may partially block the pore throat in the coal medium. The two mechanisms account for the formation of micropore at the expense of mesopore in the coals after S_CCO_2 exposure. An increased amount of the micropore is larger than the decreased amount of the mesopore, implying that the combined influence of the two mechanisms results in an increased amount of the adsorptive pore.

3.2.3. Pore Size Distribution Determined by Low-Pressure N₂ and CO₂ Sorption

The mesopore volume distribution of the raw and ScCO₂-treated coal samples derived from BJH model are presented in Figure 8. The results indicate that the PSD of raw and ScCO₂-treated coal samples show multimodal distribution in the mesopore range. According to Figure 8, contact with ScCO₂ does not change the profile of PSD significantly in the mesopore range for various rank coals. However, the major peaks for ZL, GY, and DT coal were weakened after ScCO₂ exposure. This observation is consistent with Gathitu et al. [37], who revealed that the mesopores in coal matrix may collapse during the interaction with ScCO₂, resulting in a decrease of the mesopore amount in the coal mass. According to Figure 8, pore size distributions are very similar for GY and DT coal at >5 nm, a potential effect of the similar ranks of GY and DT coal.



Figure 8. Pore size distribution (PSD) for the raw and ScCO₂-treated coal samples determined by N₂ adsorption: (**a**) DL coal; (**b**) ZL coal; (**c**) GY coal; (**d**) DT coal.

The micropore size distribution of the raw and ScCO₂-treated coal samples was determined by nonlocal density functional theory (NLDFT), an effective method to calculate pore size 0.5–1 nm; results are shown in Figure 9. In contrast with a similar mesopore size distribution before and after ScCO₂ exposure, the micropore size distribution differs between the raw and ScCO₂-treated coal samples, indicating a change in micropore morphology after ScCO₂ exposure. The pore width of the raw coal samples shows unimodal distribution with major peaks at 0.80–0.88 nm; in contrast, the pore width of ScCO₂-treated coal samples shows multimodal distribution with major peaks at around 0.59–0.65 nm, 0.75–0.8 nm, and 0.82–0.85 nm. This implies that a new micropore formed in various

rank coals with $ScCO_2$ exposure. As mentioned above, this can be interpreted by micro-fracturing of the coal matrix with $ScCO_2$ exposure. Pan et al. [38] further indicated that many closed pores in the raw coals opened and transmitted to adsorption pore with $ScCO_2$ exposure, resulting in an increase of micropore connectivity.



Figure 9. PSD for the raw and ScCO₂-treated coal samples determined by CO₂ adsorption: (**a**) DL coal; (**b**) ZL coal; (**c**) GY coal; (**d**) DT coal.

3.3. Effect of Sc-CO₂ Exposure on High-Pressure CO₂ Adsorption

The high-pressure adsorption isotherms of CO_2 on the raw and $ScCO_2$ -treated coal samples are shown in Figure 10. All the isotherms belong to type I, indicating an occurrence of monolayer adsorption [30]. Figure 10 shows that, although $ScCO_2$ exposure does not change the shape of the adsorption isotherms for CO_2 adsorption, it significantly affects the adsorption capacities of various rank coals. Notably, $ScCO_2$ exposure can enhance CO_2 adsorption at a low pressure; however, the CO_2 adsorption capacity for all the $ScCO_2$ -treated samples is lower than the raw coal samples at higher pressure. This may be the combined effects of surface property and pore structure alterations for the coal samples with $ScCO_2$ exposure. At a low pressure, the adsorption capacity is mainly dominated by the micropore; the increase of micropore volume leads to higher adsorption capacity after $ScCO_2$ exposure. The adsorption transferred to the mesopores at a higher pressure whereas a decrease in mesopore volume resulted in lower adsorption capacity. In addition, the density of surface functional groups on coal surface can promote CO_2 adsorption [39,40]. Thus, the extraction of functional groups on the coal surface by $ScCO_2$ may be another reason for the decrease of CO_2 adsorption capacity at a higher pressure.

To describe the high-pressure adsorption isotherms of CO_2 on various rank coals before and after $ScCO_2$ exposure, the Langmuir model, which is based on monolayer adsorption, is employed, which was given as:

$$n = \frac{n_m b p}{1 + b p} \tag{1}$$

where *n* is adsorbed amount, *p* is the equilibrium pressure, n_m is monolayer adsorption capacity, also known as Langmuir volume, and *b* is a constant known as Langmuir constant [41].

The fitting parameters for the isotherms were determined by Origin Lab software and the best-fit results are summarized in Table 3. The adsorption isotherms were well fitted by Langmuir with R^2 greater than 0.99 for all cases. The values of n_m for the raw coals are larger than the ScCO₂ treated coals, as seen in Figure 11a, indicating a decrease of monolayer ability after ScCO₂ exposure. As mentioned above, this may be due to the reduction of the surface functional group density with ScCO₂ exposure. Unlike n_m , the values of *b* for the coal samples were increased, as seen in Figure 11b, suggesting that the monolayer ability can be attained at a lower pressure after ScCO₂ exposure.



Figure 10. Adsorption isotherms of CO_2 on the raw and $ScCO_2$ -treated coal samples at 40 °C and the fitting curves by Langmuir model: (**a**) DL coal; (**b**) ZL coal; (**c**) GY coal; (**d**) DT coal.

Sample	State	$n_{ m m}/ m mmol\cdot g^{-1}$	В	R^2
DL coal	raw coal	0.102	2.923	0.9993
	ScCO ₂ -treated	0.092	4.056	0.9954
ZL coal	raw coal	0.181	0.416	0.9991
	ScCO ₂ -treated	0.110	0.906	0.9975
GY coal	raw coal	0.243	2.538	0.9990
	ScCO ₂ -treated	0.211	4.050	0.9964
DT coal	raw coal	0.202	1.994	0.9981
	ScCO ₂ -treated	0.163	5.029	0.9960

Table 3. Fitting parameters of the Langmuir model for CO₂ adsorption at 40 °C.



Figure 11. Fitting parameters for Langmuir model: (a) $n_{\rm m}$; (b) b.

3.4. Implications for CO₂ Sequestration in Coal Seams for Coal Seam Gas (CSG) Enhancement

To date, several projects of ECBM have been carried out in USA, Canada, China, Japan, and Australia. A comprehensive understanding of the effects of $ScCO_2$ exposure on coal seams during the storage is essential to predict the feasibility of these projects [42]. On the basis of the results of this study, $ScCO_2$ will significantly influence the surface property pore structure as well as high-pressure CO_2 adsorption capacity in the coal seam during long-term storage. These effects may be aggravated during in-situs conditions, due to the combined effect of $ScCO_2$ and the seam water. Thus, field-scale reservoir tests are still needed to better understand the response of coal seams to CO_2 sequestration.

4. Conclusions

In this study, the alterations of surface property and pore structure as well as the corresponding high-pressure CO_2 adsorption capacity in various rank coals were experimentally studied on raw and ScCO₂-treated coal samples (T = 40 °C, P = 16 MPa). The major conclusions are summarized as follows:

- (1) For various rank coals, the density of the surface functional groups and inorganic corresponds decreased after ScCO₂ exposure due to the dissolution and extraction effect of ScCO₂;
- (2) The interaction with ScCO₂ has a minimal influence on pore shape of various rank coals. The micropore SSA and pore volume were increased while values for mesopore decreased;
- (3) The combined effects of surface property and pore structure alterations lead to a higher CO₂ adsorption capacity at a low pressure but a lower CO₂ adsorption capacity at a high pressure;
- (4) The adsorption isotherms of the raw and ScCO₂-treated coals can be well described by Langmuir model. The monolayer capacity of the various rank coals decreased after exposure to ScCO₂, indicating an elimination of the adsorption sites with ScCO₂ exposure.

Finally, it can be concluded from the results of this study that $ScCO_2$ exposure has a distinct influence on the surface property, pore structure, and high-pressure CO_2 adsorption capacity of the coals, irrespective of its rank.

Author Contributions: Z.Z. and Z.L. conceived and designed the experiments; Z.L. performed the experiments; Z.L. and T.W. analyzed the data; Z.Z. and X.L. contributed materials and analysis tools; Z.L. and X.D. wrote the paper.

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