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The effect of small micropores on methane adsorption of coals from Northern China

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Abstract In this study, the effect of coal micropores on the adsorption properties, especially the Langmuir pressure (P_L), was investigated by testing 11 coal samples from Northern China. The adsorption of CO_2 at 273 K was utilized to analyze the pore size distribution. The results of these coals show that micropore volume and micropore surface area are the major factors affecting the Langmuir volume (V_L) but have weaker effects on P_L. Micropore filling theory considers that some smaller micropores with an obvious overlapping adsorption force cause volume filling adsorption. These micropores firstly reach saturated adsorption, controlling the adsorption volume at the low-pressure stage and thus have a great effect on P_L. Four times the methane molecular diameter, 1.5 nm, was assumed as the critical pore size with obvious overlapping adsorption force. The relationship between P_L and the proportion of the pore volume below 1.5 nm to the micropore volume was investigated, and it was found that the higher the volume proportion of these small micropores was, the smaller the P_L was, though two data points deviated from this trend. The reason for the anomalous coal samples could be the deviation from the assumed critical pore size of 1.5 nm for volume filling and the effects of the various micropore surface properties, which await further study.

The micropore surface increases with increasing coal rank, as does V_L. The proportion of pore volume below 1.5 nm increases with coal rank, and P_L reverses. However, these relationships are discrete.

Keywords Langmuir volume · Langmuir pressure · Micropore filling theory · Pore size distribution · Coal rank

Notation

V_L:	Langmuir volume [mL/g]
P_L:	Langmuir pressure [MPa]
P:	Pressure [MPa]
V:	Volume [mL]
ad:	air dried basis
daf:	dry ash-free basis
$R_{o,\max}$:	Mean maximum reflectance of vitrinite [%]

1 Introduction

Coal gas is a major contributor to coal mine outbursts (Valliappan and Zhang 1999; Jacek 2011) and can be exploited as a source of natural gas (Boyer and Bai 1998). A knowledge of coal gas adsorption characteristics is important for the control of gas disasters and the exploitation of coal gas.

The most widely used equation for the adsorption isotherm of coal is the Langmuir equation, $V = V_L P/(P + P_L)$. The Langmuir volume V_L represents the so-called monolayer adsorption capacity of coal assumed as the maximum adsorption capacity, and the Langmuir pressure P_L represents the adsorption pressure P when the adsorbed volume V reaches half the Langmuir volume V_L. Based on some hypotheses, the Langmuir equation describes monolayer adsorption on open surfaces freely exposed to gas (Langmuir 1918). Although the Langmuir equation cannot reflect the true adsorption mechanism of coal, it fits the I type adsorption isotherm well, as classified by IUPAC (1985) and adequately models the coal adsorption isotherm, which generally shows a I type adsorption isotherm (Ruppel et al. 1974). The Langmuir parameters could artificially

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reflect the adsorption characteristics of coal gas on coal and the clear knowledge of their influencing factors is necessary for governing coal gas.

As a naturally porous material, coal has widely distributed pore sizes: micropores ($<$2 nm), mesopores (2 nm $<$ diameter $<$ 50 nm) and macropores ($>$ 50 nm) (IUPAC 1994). Previous researches have demonstrated that coal maceral and rank have major effects on the pore size distribution. Lots of investigation on pore size distribution of different coal macerals proved that vitrinite has more micropores than inertinite, and exinite has the least (Harris and Yust 1979; Unsworth et al. 1989; Clarkson and Bustin 1996; Crosdale et al. 1998; Mastalerz et al. 2008). The variety of pore distribution, especially the micropores would lead to the difference in adsorption capacity. It is the response that most research shows that vitrinite-rich coals with more micropores have a higher adsorption capacity than inertinite-rich coals (Lamberson and Bustin 1993; Bustin and Clarkson 1998; Crosdale et al. 1998; Clarkson and Bustin 1999; Dutta et al. 2011). For various rank coals, the investigations by Gan et al. (1972) and Spitzer (1981) showed that the porosity of low and medium-rank coals was mostly due to larger pores than higher rank coals, confirmed by the observation of Prinz and Littke (2005). The increasing rank of moisture-equilibrated coals led to the increase of the Langmuir volume (Levy et al. 1997), while dry coals showed second-order polynomial trends with increasing rank (Laxminarayana and Crosdale 1999; Levy et al. 1997; Dutta et al. 2011).

However, most previous research has focused on the factors affecting the Langmuir volume V_L, placing much less attention on the Langmuir pressure P_L. Laxminarayana and Crosdale (1999) have found a strong relationship of decreasing P_L with increasing rank and suggested the cause of less heterogeneous pore surfaces with increasing rank. Dutta et al. (2011) observed a U-shaped trend between P_L with increasing rank. As one of the two Langmuir constants, P_L indicates adsorption volume increase speed with increasing gas pressure, which is of important significance to the resource and output estimate of coalbed methane (Pashin 2010) and to the prediction of methane releasing in coal mining. To make sure the factors on P_L, more work is needed. The variety of coal pores characterizes the adsorption and brings the complexity for research. The study by Bustin and Clarkson (1998) indicated that micropore structure of coal was the controlling factor on adsorption of gas. In this paper, the effects of micropores on the adsorption characteristics, especially on P_L, are analyzed.

2 Methods

2.1 Coal samples and preparation

Eleven coal samples were selected from the following mines in Northern China: Wolonghu Mine, Haizi Mine and Qinan Mine of Huaibei City in Anhui Province, the Fourth Mine of the Pingyu Ming Group and Jiulishan Mine of Jiaozuo City in Henan Province, Hongling Mine of Shenyang City in Liaoning Province and Pangzhuang Mine of Xuzhou City in Jiangsu Province. The detailed sampling area and mark labels of these coal samples are shown in Table 1.

After sampling, the coal samples were crushed. Approximately 10 g of the coal samples 0.074–0.2 mm in size were sifted for proximate analysis and approximately 100 g of the coal samples 0.2–0.25 mm in size were sifted for petrographic analysis, methane adsorption test and CO_2 adsorption test.

Table 1 Proximate analysis and adsorption testing results

Sample	Sampling location	Moist (wt.%, ad)	Ash (wt.%, ad)	Volatile matter (wt.%, daf)	Fixed carbon (wt.%, ad)	V_L (cc/g, daf)	P_L (MPa, daf)
H7	Haizi Mine coal seam 7	2.52	42.81	13.65	47.23	36.94	0.96
H8	Haizi Mine coal seam 8	0.84	24.95	26.22	54.76	24.46	1.63
H9	Haizi Mine coal seam 9	1.49	20.08	11.99	69.03	41.05	1.00
H10	Haizi Mine coal seam 10	0.99	9.95	13.12	77.38	26.81	0.87
W102	Wolonghu Mine coal seam 10	3.62	35.56	12.70	53.10	56.53	0.62
P	The Fourth Mine of Pingyu Ming Group coal seam 2	1.16	14.90	16.91	69.90	33.77	1.34
J6	Jiulishan Mine coal seam 5	3.61	8.10	7.45	81.72	49.44	0.87
J5	Jiulishan Mine coal seam 2	3.30	14.01	12.55	72.32	43.66	0.73
HL7	Hongling Mine coal seam 2	1.01	18.68	18.31	65.61	27.81	0.70
Q3	Qinan Mine coal seam 3	1.40	16.56	40.25	49.02	16.11	1.12
P9	Pangzhuang Mine coal seam 9	1.97	19.71	36.71	49.58	15.79	0.79

2.2 Proximate analysis

Following the MT/T 1087-2008 test methods for proximate analysis of coal by instruments, we used 5E-MAG6600 for proximate analysis through thermogravimetric analysis (China State Administration of Work Safety 2009).

2.3 Petrographic analysis

Following the GB/T 16773–2008 method of preparing coal samples for coal petrographic analysis (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and Standardization Administration of the People's Republic of China 2008a), we prepared polished sections with coal samples of 0.2–0.25 mm in size for determination of the maceral group composition and minerals and the reflectance of vitrinite in coal. We determined the maceral group composition and minerals in the coal according to the GB/T 8899–1998 method (State Bureau of Quality Technology Supervision of the People's Republic of China 1998). The maximum reflectance of vitrinite in the coal samples was determined in accordance with the GB/T 6948–2008 method for microscopically determining the reflectance of vitrinite in coal (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and Standardization Administration of the People's Republic of China 2008b).

2.4 Methane adsorption test

Using high-pressure volumetric equipment based on the theory of static volumetric determination described by Sing et al. (1982), we tested the methane adsorption isotherm of dry coal according to the MT/T752-1997 method for determining the methane adsorption capacity in coal (China Department of Coal Industry 1997). Approximately 50 g of a coal sample 0.2–0.25 mm in size was weighed and placed in a vacuum drying oven. After drying at 378 K under 4 Pa for 2 hours, the sample was cooled to room temperature and then placed in the coal sample tank with the measured volume for evacuation under 4 Pa for 8 hour at 333 K. Then, we tested the adsorption at 303 K by the volumetric method. The coal sample tank was linked to a reference tank with the measured volume. From the pressure changes of the reference tank, the volume of methane entered the coal sample tank could be obtained according to the state equation of real gas. In the same way, the volume changes of free gas in the coal sample tank could be obtained by its pressure changes when the adsorption was balanced. And then the adsorption volume can be obtained by subtracting the free volume from the incoming volume.

2.5 Analysis of pore size distribution

For characterizing porous materials, the adsorption of N_2 at low temperature (77 K) is the most widely used technique but is limited for micropores due to the existence of diffusional problems at low temperature, whereas adsorption of CO_2 at 273 K can work as complement (Lozano-Castello et al. 2004). An AUTOSORB-1 instrument produced by Quantachrome Instruments Co., Florida, USA, was used for CO_2 adsorption at 273 K on coal samples of 0.2–0.25 mm in size.

For analysis of micropores, Marsh (1987) suggested that the Dubinin-Radushkevich (DR) equation (Dubinin 1960) and the Dubinin-Astakhov (DA) equation (Dubinin and Astakhov 1971) based on the micropore filling mechanism were superior to the Langmuir and BET equations for differentiation and description of micropores in coal and carbon materials. The DR and DA methods provided by the AUTOSORB-1 program were adopted for the analysis of CO_2 adsorption at 273 K.

3 Result and discussion

3.1 Proximate analysis and adsorption testing results

The results of proximate analysis and the Langmuir constants for methane adsorption are shown in Table 1, and the adsorption results and the fitting Langmuir curves are shown in Fig. 1. Volatile matter decreased from 40.25 % to 7.45 %. The Langmuir volume increased from 15.79 mL/g to 56.53 mL/g, and the Langmuir pressure increased from 0.62 MPa to 1.63 MPa with both parameters having large spans.

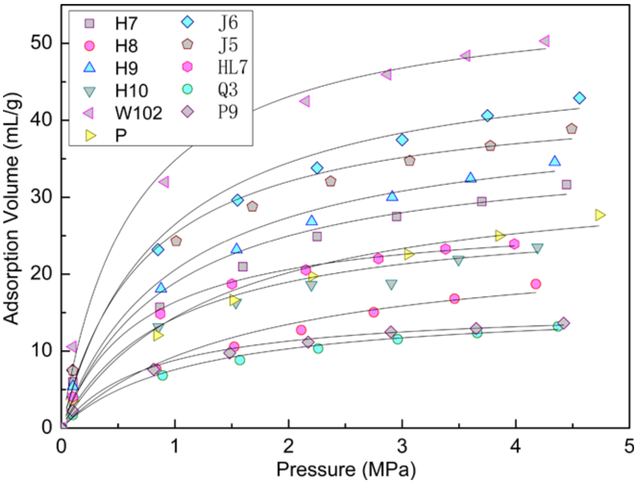

Fig. 1 Methane isothermal adsorption results and the fitting Langmuir curves

Table 2 Petrographic analysis results

Sample	Vitrinite (%)	Inertinite (%)	Exinite (%)	Mineral (%)	$R_{o,\max}$ (%)	Coal rank
H7	82.95	11.6	0	5.454	2.36	anthracite C
H8	85.7	7.25	0	7.05	1.41	bituminous A
H9	86.1	9.5	0	4.4	2.00	anthracite C
H10	84	12.5	0	3.5	2.24	anthracite C
W102	70.2	26.5	0	3.3	4.06	anthracite A
P	86.7	8.25	0	5.05	1.90	bituminous A
J6	91.3	5.5	0	3.2	2.13	anthracite C
J5	83.35	8.25	0	8.4	1.60	bituminous A
HL7	91.25	5.5	0	3.25	2.34	anthracite C
Q3	87.7	5.25	0	7.05	0.82	bituminous C
P9	89.35	5.25	1.25	4.15	0.86	bituminous C

Table 3 Micropore size analysis determined by DR method

Sample	DR method micropore volume (mL/g)	DR method micropore surface (m^2/g)	DR method micropore width (nm)
H7	0.0082	23.46	1.23
H8	0.0014	3.98	1.25
H9	0.0111	31.71	1.25
H10	0.0075	21.48	1.22
W102	0.0211	60.44	1.25
P	0.0067	19.33	1.21
J6	0.0175	50.18	1.18
J5	0.0167	47.77	1.21
HL7	0.0054	15.44	1.24
Q3	0.0014	3.94	1.12
P9	0.0024	6.77	1.17

3.2 Petrographic analysis results

The results of maceral group composition and minerals and the mean maximum reflectance of vitrinite in the coal are given in Table 2. These samples were mainly composed of vitrinite. The mean maximum reflectance ranged from 0.82 % to 4.06 %, and the coal rank ranged from bituminous C to anthracite A according to ISO 11760:2005 (ISO 2005).

3.3 Analysis of micropore size distribution

The micropore surface area, micropore volume and the average pore size as determined by the DR method are shown in Table 3. The micropore surface area is well correlated with the micropore volume by the DR method but is poorly correlated with the average pore size. The pore size distributions as determined by the DA method are shown in Fig. 2.

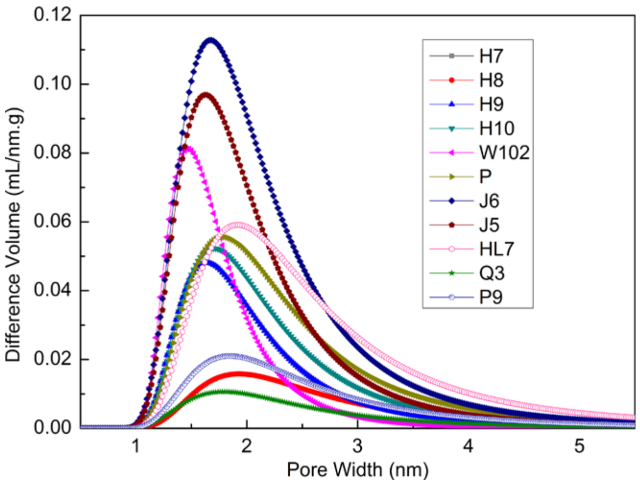

Fig. 2 Micropore size distribution as determined by the DA method

3.4 Effects of the micropore size distribution on adsorption

The Langmuir volume displayed a good correlation with the micropore surface area and the micropore volume as determined by the DR method (Figs. 3(a) and 3(b)). The linear increase of V_L with the micropore surface area and the micropore volume indicates that micropore in coal is the governing factor on V_L. Whether the monolayer adsorption in large micropores or the volume filling adsorption in small

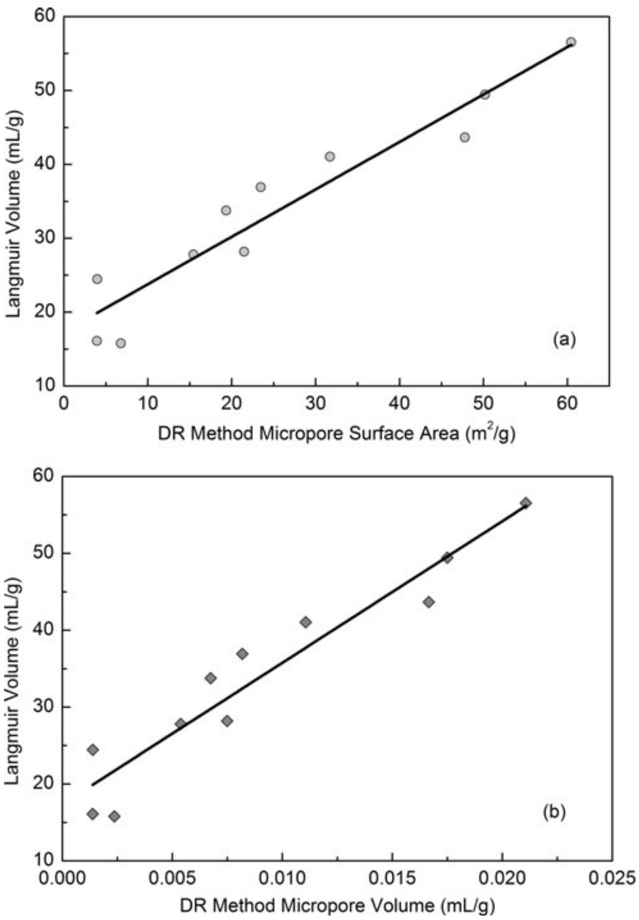

Fig. 3 Relationship between the Langmuir volume and the micropore surface area (**a**) and the micropore volume (**b**) as determined by the DR method

micropores, the increase of the micropore surface area and the micropore volume enhance the maximum adsorption capacity virtually represented by V_L.

The Langmuir pressure (P_L) shows differences from V_L. The P_L shows unobvious decreasing trends with the micropore volume and the micropore surface as determined by the DR method (Figs. 4(a) and 4(b)). The insensitivity of P_L to surface area indicates that the micropore surface area is not the key factor affecting P_L. P_L represents the adsorption pressure P when the adsorbed volume V reaches half the maximum adsorption volume, and the adsorption volume at low pressure will have great effect, which is affected by the adsorption potential for a certain adsorption gas. This effect can hardly be explained through Langmuir adsorption theory with the hypothesis of invariable adsorption heat.

Micropore filling theory (Dubinin 1960) based on adsorption potential theory is suitable for the description of adsorption in micropores. Clarkson et al. (1997) has verified the validity of adsorption potential theory by analyzing the methane adsorption isotherm of coal between 0–10 MPa at 298–323 K. The micropore filling mechanism considers the effect of increasing adsorption potentials as a result of overlapping of the fields of opposite pore walls. The potential profile of N_2 molecules adsorbed in a slit-like pore by Kaneko (1996) demonstrates that the maximum adsorption potential forms in smaller micropores, and two maximum adsorption potentials form as the distance of the pore wall increases. The adsorption potential decreases with increasing pore size but is still larger than that of a single pore wall. The further study of the micropore filling mechanism by Carrott et al. (1987) divides it into two stages: the primary stage at a lower relative pressure ($p/p_0 < 0.01$) in micropores with widths similar to gas molecular diameter and then the secondary process with the synergistic effect of adsorbent and adsorbate at a relative pressure of $p/p_0 \approx 0.01$–0.2. Kakei et al. (1990) demonstrated this two-stage pattern and proposed a multistage pattern characterized by an L stage, M stage and H stage.

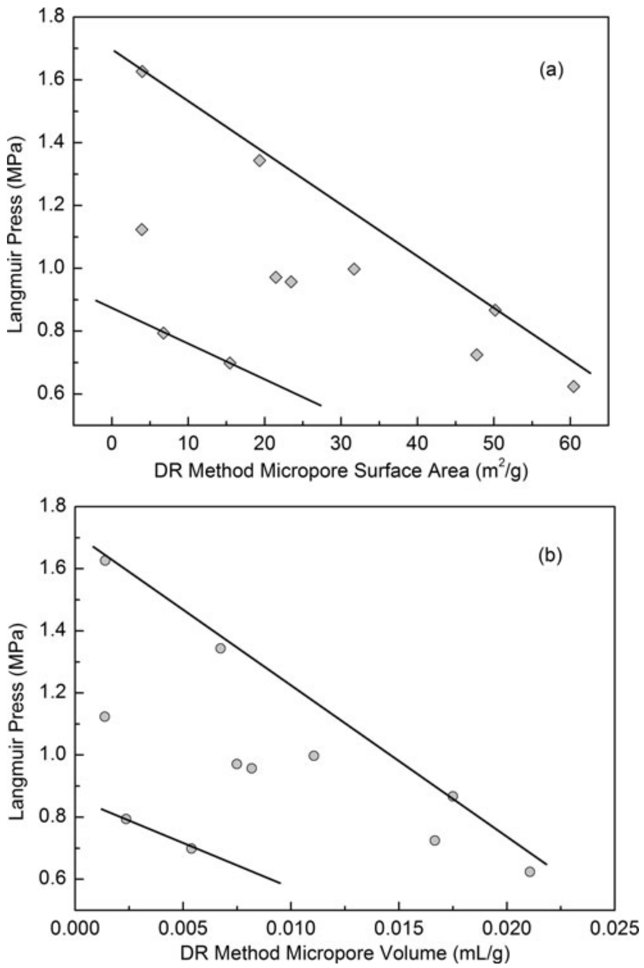

Fig. 4 Relationship between the Langmuir pressure and the micropore surface area (**a**) and the micropore volume (**b**) as determined by the DR method

The molecular diameter of methane is 0.38 nm (Cracknell et al. 1993). According to the multistage filling process by Kakei et al. (1990), L-stage micropore filling occurs in pores of one to two times the gas molecular diameter (0.38–0.76 nm for methane), M-stage micropore filling occurs in pores of three to four times the gas molecular diameter (1.14–1.52 nm for methane), and H-stage micropore filling will occur on the mono-adsorbed layer as the adsorption pressure increases. For larger pores, the effect of increasing adsorption potentials by overlapping is very little, and the adsorption potential is close to that of an open surface, occurring by polymolecular layers or monolayer adsorption. In other words, gas uptake on coal can be characterized by a dual mechanism, the multistage filling process for absorption into micropores and polymolecular layers or monolayer adsorption on surface for larger pores. A detailed adsorption process on activated carbon simulated through Grand canonical Monte Carlo (GCMC) simulation has shown an obvious delay in decreasing potential energy until 1.52 nm (Cao et al. 2002), which is correlated with the L and M stages of the multistage filling mechanism.

Micropores with a remarkable superimposed adsorption potential can reach saturation adsorption at low pressure. These micropores control adsorption volume at low pressure as well as the proportion of the maximum adsorption volume and thus have a key effect on the Langmuir pressure (P_L). The adsorption energy profile between an adsorbate molecule and a slit-shape micropore by X. Cui et al. (2004) showed that strong enhancement of the adsorption energy begins when the pore size becomes smaller than four times the gas molecular diameter. Thus, we assumed 1.5 nm, four times the methane molecular diameter, as the critical pore size with obvious overlapping adsorption force; if these smaller micropores account for a large proportion of micropores, the adsorption volume rises sharply at low pressure, indicating a small P_L. Connecting the pore size distribution points in Fig. 2, the cumulative area is the pore volume. The relationship between P_L and the volume proportion of small micropores to the total micropores is shown in Fig. 5. From this figure, we can see the decreasing trend of P_L with increasing proportion. The relationship between P_L and the small micropores indicates small micropore is one dominating influencing factor. However, there are two outlying points, HL7 and P9, without which the related coefficient reaches 0.876. The value of P_L does not entirely agree with the proportion of pore volume below 1.5 nm. On the one hand, micropore-filling critical pore size of 1.5 nm is the default size; on the other hand, the pore surface properties, such as the distribution of functional groups, affect the methane adsorption force. For a comprehensive and clearer cognition, more study is still necessary.

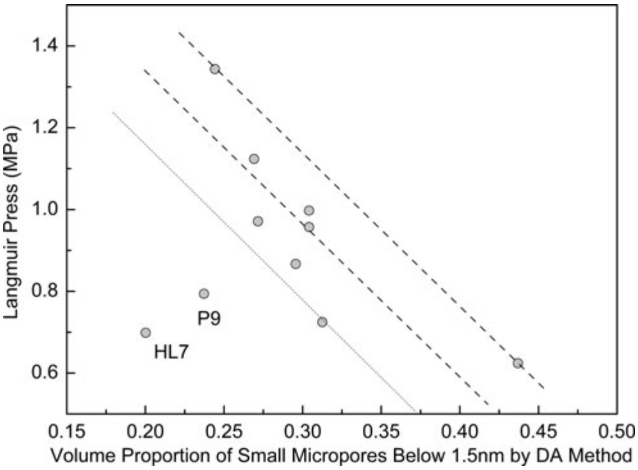

Fig. 5 Relationship between the Langmuir pressure and the proportion of pore volume below 1.5 nm to the total micropore volume

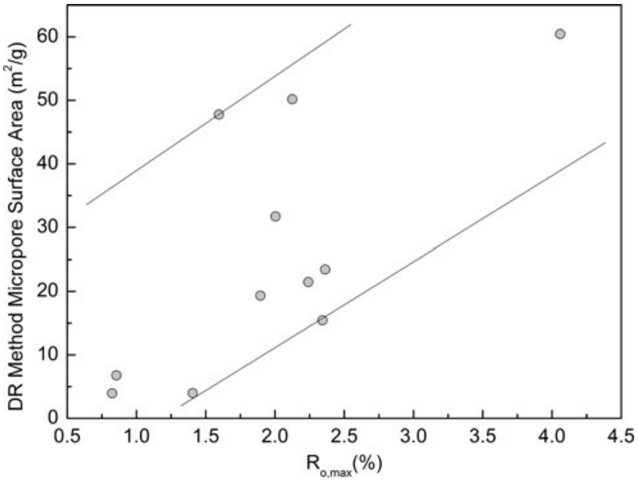

Fig. 6 Relationship between the micropore surface area as determined by the DR method and coal rank

3.5 Effect of coal rank on micropores and adsorption properties

Coal rank has important effects on micropores and adsorption properties. As Fig. 6 shows, the micropore surface area increases with increasing coal rank, but the relationship is discrete to a certain degree. We can see a similar relationship between the Langmuir volume and coal rank from Fig. 7 which is different from previous investigation (Prinz and Littke 2005). The proportion of pore volume below 1.5 nm increases with coal rank, and the Langmuir pressure reverses, despite some discreteness (Figs. 8 and 9). Although the strong relationship between P_L and coal rank was not found (Fig. 9), we suggest that the cause is partly related to the increasing micropores with increasing rank, especially the small micropores.

4 Conclusion

Micropores are the key factor affecting coal adsorption. The micropore surface and volume have dominating effect on the

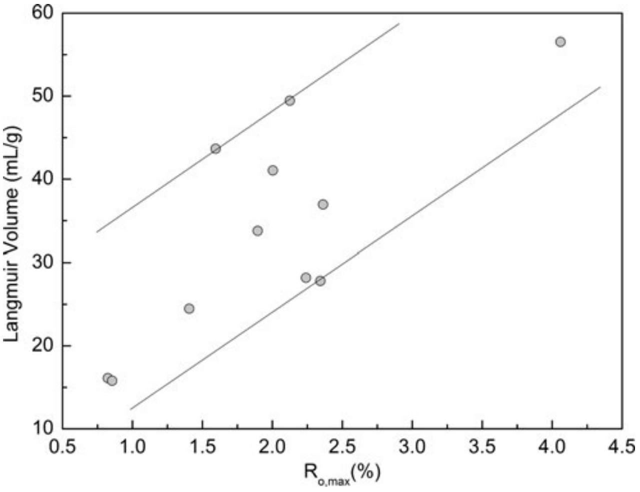

Fig. 7 Relationship between the Langmuir volume and coal rank

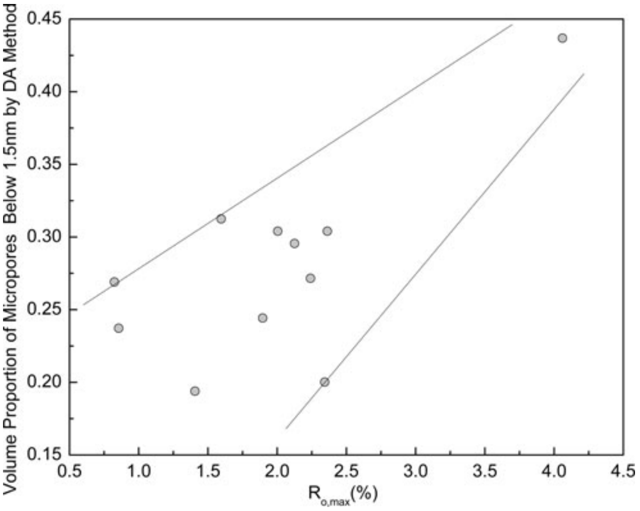

Fig. 8 Relationship between the proportion of pore volume below 1.5 nm and coal rank

Langmuir volume (V_L). A larger micropore surface or volume corresponds to a larger V_L. The micropore volume and surface have a weaker effect on the Langmuir pressure (P_L). Pores in which the volume filling of micropores occurs reach saturation adsorption at low pressure, resulting in a sharp increase in the adsorption volume and thus controlling the P_L. We assumed 1.5 nm, four times the methane molecular diameter, as the critical pore size for obvious overlapping adsorption force and analyzed the relationship of P_L to the pore volume below 1.5 nm and found that P_L decreased with the increasing proportion of these small micropores volume to the micropore volume except in the cases of two samples, HL7 and P9. The reason for the outlying coal samples could be a deviation from the assumed critical pore size of 1.5 nm for volume filling or the effects of various micropore surface properties. These possibilities await further study.

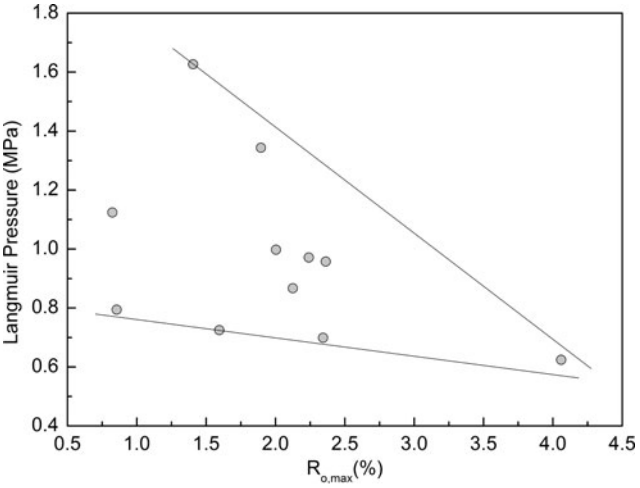

Fig. 9 Relationship between the Langmuir pressure and coal rank

Coal rank is an important factor affecting the micropore size distribution and thus has an effect on coal adsorption. The micropore surface increases with increasing coal rank as does the Langmuir volume. The proportion of pore volume below 1.5 nm increases with coal rank, and the Langmuir pressure reverses. However, these relationships are discrete.

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