Influence of pore width on adsorption capacity of shale: Insights from high pressure adsorption experiments on model substances

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Abstract. Shale gas has become an important unconventional resource worldwide and adsorbed gas mainly contribute to the initial gas content for shale. In this study, different model substances, including 3Å molecular sieve, 4Å molecular sieve, 5Å molecular sieve and 13X molecular sieve, were conducted by high pressure methane adsorption experiments and the results were analyzed to obtain the effect of pore width on methane adsorption capacity. The results show that methane molecular almost cannot enter the pore of 3Å molecular sieve for adsorption, only adsorption on surface can be occurred, as well as the pore of 4Å molecular can be slightly entered by methane molecular. Whereas, methane molecular can totally enter the pore of 5Å and 13X molecular for adsorption. Meanwhile, at low pressure (less than 1.0MPa), the excess adsorption amount of methane for 13X is slightly greater than that of 5Å molecular sieve. With the increasing of pressure (1-18MPa), the excess adsorption amount of methane for 5Å is greater than that of 13X molecular sieve. In the pressure ranging from 18 to 30MPa, the excess adsorption amount of methane for 13X is greater than that of 5Å molecular sieve.

1. Introduction
Shale gas has become an important unconventional resource worldwide. Recently, in petroliferous basins of China, shale gas has also gained significant breakthroughs[1-2]. It is well accepted that the adsorbed gas on pore surfaces in organic matter and inorganic materials, free gas in cracking and dissolved gas in liquid generated hydrocarbon are three primary occurrence states for shale gas[3-4]. In general, the adsorbed gas in shale gas ranges from 20% to 85%, revealing that adsorbed gas mainly contribute to the initial gas content for shale[5]. Methane isothermal adsorption experiments were conducted for different shale samples to obtain the adsorption capacities and its influencing factors[6-9]. The results show that total organic carbon (TOC) content has an obvious positive relationship with adsorption capacity of shale.

The relationship of pore width and adsorption potential has been established in previous studies[10-12]. In general, interaction cannot be discovered in gas molecular and pore wall with ratio of pore radius (R) to dynamics diameter of molecular (σ) at 3.0. In addition, the previous study reveals that the interaction of gas molecules with pore width increases with decreasing pore width and reached the peak at ratio of R to σ at 1.086 for cylindrical-shape pore and at 1.0 for slit-shape pore, suggesting that the methane adsorption capacity varies in adsorption materials with different pore width.

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distributions[10]. Molecular simulations were conducted in previous study to investigate the pore size effects on adsorption[13], the results reveal the adsorption ratio can be 100% in pore width less than 1.24nm in molecular simulation. However, no previous study focused on the experiential investigation of pore width on methane adsorption capacity of materials, hindering the deep understanding of alkane gases adsorption in shale.

In this study, different model substances, including 3Å, 4Å, 5Å and 13X molecular sieves, were conducted by high pressure methane adsorption experiment and the results were analyzed to obtain the effect of pore width on methane adsorption capacity.

2. Samples and experiments

2.1 Samples

In this study, different model substances, including 3Å, 4Å, 5Å and 13X molecular sieves, were obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD. Generally, the above model substances are alkali metal aluminosilicate with different pore sizes. The average pore size of 3Å, 4Å, 5Å and 13X molecular sieves are about 0.3nm, 0.4nm, 0.5nm and 1.0nm, respectively.

2.2 Experiments

The high pressure methane adsorption measurements were finished by a magnetic suspension balance ISOSORP-HP Static II (Rubotherm GmbH, Germany). The pressure was measured from 0 to 30MPa and the temperature was set to 60°C. The measurement process includes four steps: firstly, the blank measurement, which was conducted to determine the mass and volume of the sample container by using the N₂ gas. Secondly, the pretreatment. The sample were crashed to 80 meshes and loaded to the sample container, then carrying out the measurement process under vacuum & 105°C for 4h in order to remove the possibly sorpted elements including water and other gases. Thirdly, the buoyancy measurement, which was conducted to determine the mass and the volume of sample by using the helium gas. Lastly, the sorption measurement, which was conducted by the methane pressure increased from 0 to 30MPa at 60°C with equilibrium time of ~2h at every assigned pressure segment. Therefore, the \( \frac{\Delta M}{\Delta P} \) sorption curve at the iso-temperature can be obtained after calibration of buoyancy measurement.

3. Results and discussions

3.1 The characteristics of methane adsorption isotherms

The measured excess adsorbed methane can be calculated by weight varying in high pressure methane adsorption measurement as following:

\[
m_{ex} = m_{blance} + \rho_g(P,T) \cdot V_{container+sample} - m_{container+sample}
\]

Measured excess methane adsorption isotherms of different materials at 60°C were presented in Figure 1. In 3Å molecular sieve (Figure 1(a)), the measured excess methane adsorption \( n_{ex} \) were initially negative value and negatively increased with increasing pressure. In 4Å molecular sieve (Figure 1(a)), the \( n_{ex} \) increased at low pressure with the initially positive value and peaked at 1.0MPa. Then, the \( n_{ex} \) decreased to zero at about 4MPa, afterwards, the \( n_{ex} \) negatively increased with increasing pressure. However, 5Å and 13X molecular sieve show a different adsorption characteristic (Figures 1(b)). For 5Å molecular sieve, the \( n_{ex} \) increased with increasing pressure and peaked at 8.0MPa with \( n_{ex} \) of 33.83mg/g. Then, the \( n_{ex} \) decreased to 22.15mg/g at the final experimental pressure segment (30MPa). For 13X molecular sieve, the \( n_{ex} \) increased with increasing pressure and peaked at 10.0MPa with \( n_{ex} \) of 32.32mg/g. Then, the \( n_{ex} \) decreased to 23.25mg/g at final experimental pressure segment (30MPa).
Figure 1. Measured excess methane adsorption isotherms of different materials at 60°C.

It is well accepted that the diameter of Helium and methane molecules are 0.26 nm and 0.38 nm respectively, indicating that the entered pore width range for above two gas molecules are different. The average pore width of 3 Å and 4 Å molecular sieve is 0.3 nm and 0.4 nm, respectively. Therefore, the methane molecular cannot enter pore of 3 Å molecular sieve for adsorption, only adsorption on surface can be occurred. Previous study reveals that ratio of R to σ less than 0.85 can lead to a positive adsorption energy, revealing the gas molecular can no longer enter the pore for adsorption[14]. For 4 Å molecular sieve, the pore width is close to diameter of methane molecule (0.38 nm) and the ratio of R to σ is 0.52, indicating that the methane molecular can slightly enter the pore of 4 Å molecular for adsorption. Therefore, the skeleton volume for samples measured by helium, which is used to calculate the buoyancy during the methane adsorption measurement, is remarkably lower, then leading that the calculated buoyancy is lower than actual buoyancy, acting as the leading factor of the negative adsorption phenomena in 3 Å and 4 Å molecular sieve. For 5 Å and 13X molecular sieves, the methane can totally enter the pore for adsorbing.

3.2 Absolute adsorption of 5 Å and 13X molecular sieve

The absolute adsorption isotherms can be fitted by Langmuir model and the fitted results for 5 Å and 13X molecular sieve were presented in Figure 2. The results show that the measured excess adsorption was well fitted with established model. However, at low pressure (less than 1.0 MPa), the excess adsorption amount of methane for 13X is slightly greater than that of 5 Å molecular sieve. With the increasing of pressure (1 to 18 MPa), the excess adsorption amount of methane for 5 Å is greater than that of 13X molecular sieve. In the pressure ranging from 18 to 30 MPa, the excess adsorption amount of methane for 13X is greater than that of 5 Å molecular sieve. Meanwhile, the maximum absolute adsorbed amounts of methane for 5 Å and 13X molecular sieves are 3.06 mmol/g and 2.76 mmol/g, respectively, suggesting that 5 Å has a greater methane adsorption capacity than 13X molecular sieve.

Figure 2. Measured and fitted excess adsorption isotherms and calculated absolute adsorption isotherms for 5 Å molecular sieve (a) and 13X molecular sieve (b).
3.3 Influence of pore width on adsorption process

Relationship of adsorption energy and half width of slit-shape pore were presented in Figure 3. The result shows that the adsorption can reach the peaks at half width of about 0.36nm. For 5Å and 13X molecular sieve, the results clearly indicate that the adsorption energy for methane in 13X molecular sieve is greater than that of 5Å molecular sieve. However, the maximum absolute adsorbed amounts of methane for 5Å molecular sieve (3.06mmol/g) is greater than that of 13X molecular sieve (2.76mmol/g), may suggesting that adsorption capacity can be jointly influenced by pore width and other factors (eg. surface area).

![Figure 3](image)

Figure 3. Relationship of adsorption energy and half width of slit-shape pore(modified from Cui et al.(2004)[14])

4. Conclusions

In this study, different model substances, including 3Å, 4Å, 5Å and 13X molecular sieve, were conducted by high pressure methane adsorption experiment. The main conclusions can be summarized as following:

(1) Methane molecular almost cannot enter the pore of 3Å molecular sieve for adsorption, only adsorption on surface can be occurred, as well as the pore of 4Å molecular can be slightly entered by methane molecular. Whereas, methane molecular can totally enter the pore of 5Å and 13X molecular for adsorption.

(2) At low pressure (less than 1MPa), the excess adsorption amount of methane for 13X is slightly greater than that of 5Å molecular sieve. With the increasing of pressure (1 to 18MPa), the excess adsorption amount of methane for 5Å is greater than that of 13X molecular sieve. In the pressure ranging from 18 to 30MPa, the excess adsorption amount of methane for 13X is greater than that of 5Å molecular sieve.

(3) Adsorption capacity can be jointly influenced by pore width and other factors (eg. surface area).

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