ORIGINAL RESEARCH ARTICLE

micron to nanometer, and macroscopic breakthroughs have become increasingly dependent on microscopic studies. Therefore, it becomes particularly important to improve our microscopic understanding by using new theories and methods (3). Moreover, the study of shale gas molecule adsorption on shale substrate surfaces helps to understand the occurrence of shale gas, to assess the gas adsorption capacity quantitatively, to explore the correlation of adsorption properties and mineral composition and to evaluate the quantity of shale gas as a natural resource.

Shale gas is generally dry and mainly consists of CH4, C2H6, CO2, N2 and other components, with the content of CH4 up to more than 95% (4, 5). The adsorption of shale gas and shale has been investigated through a large number of experimental and theoretical studies (6-12). Most of the theoretical studies show that shale gas is mainly absorbed on the surface of the kerogen and clay minerals, and is almost not adsorbed at all on the surface of calcium carbonate (13-16). Ji et al (5) studied methane adsorption on clay minerals of different sources and origins by isothermal adsorption experiment. The results showed that different types of clay minerals had evidently different gas adsorption capacities. However, there is no direct evidence of very weak gas adsorption on the surface of calcium carbonate.

ABSTRACT

Background: To demonstrate the adsorption strength of shale gas to calcium carbonate in shale matrix, the adsorption of shale gas on CaCO3 (100) surfaces was studied using the first-principles method, which is based on the density functional theory (DFT).

Methods: The structures and electronic properties of CH4, C2H6, CO2 and N2 molecules were calculated by the generalized gradient approximation (GGA), for a coverage of 1 monolayer (ML). Under the same conditions, the density of states (DOS) of CaCO3 (100) surfaces before and after the adsorption of shale gas molecules at high-symmetry adsorption sites were compared.

Results: The results showed that the adsorption energies of CH4, C2H6, CO2 and N2 on CaCO3 (100) surfaces were between 0.2683 eV and -0.7388 eV. When a CH4 molecule was adsorbed at a hollow site and its 2 hydrogen atoms were parallel to the long diagonal (H3) on the CaCO3 (100) surface, it had the most stable adsorption, and the adsorption energy was only -0.4160 eV. The change of adsorption energy of CH4 was no more than 0.0535 eV. Compared with the DOS distribution of CH4 before adsorption, it shifted to the left overall after adsorption. At the same time, the partial density of states (PDOS) curves of CaCO3 (100) surfaces before and after adsorption basically overlapped.

Conclusions: This work showed that the adsorption effect of shale gas on calcium carbonate is very weak, and the adsorption is physisorption at the molecular level.

Keywords: Adsorption energy, CaCO3 (100) surface, First-principles, Shale gas

Introduction

Shale gas, as one of the global unconventional natural gases, has received extensive attention around the world. The United States and Canada have achieved commercial exploitation of shale gas with good results. China has done a lot of work with respect to shale gas research status, reservoir mechanism and favorable-area evaluation, but the study of the adsorption of shale gas was only just initiated in recent years (1, 2). The development from conventional oil and gas fields to shale gas fields actually reflects the scale transition from

Accepted: March 17, 2017
Published online: May 29, 2017

Corresponding author:
Prof. Ping Guo
State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation Southwest Petroleum University No. 8 Xindu Avenue
Xindu District, Chengdu, PR China
guopingswpi@vip.sina.com

© 2017 The Authors. This article is published by Wichtig Publishing and licensed under Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0). Any commercial use is not permitted and is subject to Publisher’s permissions. Full information is available at www.wichtig.com
At the same time, the first-principles method is used to study the adsorption of gas molecules on material surface (17-26), but there are few reports about the adsorption of gas molecules on the surface of calcium carbonate. Based on density functional theory with solid-state nuclear magnetic resonance (SS-NMR) calculations, Bevilaqua et al (27) simulated the adsorption of hydrocarbon molecules on calcite surface (CaCO$_3$(10\(\bar{4}\))), but the adsorption of shale gas was not studied. In this paper, we adopted the first-principles method based on density functional theory (DFT) to study the adsorption stability of shale gas and its components at different high-symmetry positions on CaCO$_3$ (100) surfaces. By analyzing the adsorption results, such as the adsorption energy of gas molecules and the structure and electronic properties of CaCO$_3$ (100) surfaces, we uncovered the microscopic mechanisms of shale gas adsorption on CaCO$_3$ surfaces.

**Methods**

**Computational methods**

Based on the first-principle method of DFT (28, 29), the ground state geometries and electronic properties of CH$_4$, C$_2$H$_6$, CO$_2$ and N$_2$ molecules adsorbed on CaCO$_3$ (100) were calculated using the Cambridge Sequential Total Energy Package (CASTEP) module in Materials Studio. Within the generalized gradient approximation (GGA), Perdew-Burke-Ernzerhof (PBE) (30) exchange correlation functionals combined with ultrasoft pseudopotentials were used in the calculations. The value of plane wave cutoff energy was 300 eV. The K point grid (31) size was 3 × 1 × 1. Self-consistent field calculations were performed with a convergence criterion of 2.0 × 10$^{-6}$ eV on single atom energy. The convergence of parameters was tested for each supercell. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization algorithm proposed by Broyden, was used in the structure optimization (32-35).

**Structural models**

In this paper, the P (1 × 1) periodic supercell is used as the initial surface. Under the coverage of 1 monolayer (ML), the adsorption of CH$_4$, C$_2$H$_6$, CO$_2$ and N$_2$ on the surface was theoretically studied for each. First, an optimized CaCO$_3$ unit cell (Fig. 1) was cleaved for a (100) surface. Then a vacuum layer of 2-nm thickness was constructed to simulate the CaCO$_3$ (100) surface (Fig. 2). Finally, the CaCO$_3$ (100) structure was optimized. We focused on shale gas molecule adsorption on CaCO$_3$ (100) surfaces. Therefore, in the structural optimization computation, the position of oxygen atoms was kept on the surface layer, and the number of adsorbed of shale gas molecules was variable, whereas the atoms of the non–surface layer were immobilized. We adopted such a setting to simulate the adsorption of CaCO$_3$ on shale gas molecules in order to reduce the number of calculations and to exclude the effect of substrate thickness. The initial lattice constant of calcium carbonate was an experimental value for, a = 0.499 nm, c = 1.7061 nm (36). After optimization, the lattice constant was a = 0.499 nm, c = 1.7060 nm. The gas molecules were added on the CaCO$_3$ (100) surface to a height of 0.5 nm.
of the system before adsorption was obtained by calculating the energy of CaCO$_3$ (100) surfaces and gas molecules. Then in the same way, the total energy of the system was calculated after adsorption. The equation to calculate the adsorption energy is given by

$$
\Delta E_{ad} = E_{gas+CaCO_3} - (E_{CaCO_3} + E_{gas})
$$

Eq. [1]

where $E_{gas+CaCO_3}$ is the total energy of the system after gas adsorption, $E_{CaCO_3}$ is the energy of pure CaCO$_3$ without the gas molecule, and $E_{gas}$ is the energy of the isolated shale gas molecule. The value of $\Delta E_{ad}$ reflects the stability of the adsorption system. $\Delta E_{ad}<0$ means that the energy of the system decreases after adsorption, and the gas molecules are adsorbed. The adsorption process is exothermic. $\Delta E_{ad}>0$ means that the energy of the system increases, and the gas molecules cannot be adsorbed (37). A smaller value of $\Delta E_{ad}$ indicates better stability of the adsorption system.

Results and discussion

Analysis of adsorption energy

Table I lists the adsorption energy of CH$_4$, C$_2$H$_6$, CO$_2$ and N$_2$ molecules on CaCO$_3$ (100) surfaces in the 12 adsorption modes. CH$_4$, C$_2$H$_6$ and N$_2$ molecules had negative $\Delta E_{ad}$, and the lowest adsorption energy was -0.4160 eV, -0.7388 eV and -0.1567 eV, respectively. The adsorption capacity of 3 kinds of
First-principles calculation of adsorption of shale gas on CaCO$_3$

Gases on the surface of calcium carbonate follows the order of C$_2$H$_6$ > CH$_4$ > N$_2$. However, the $\Delta E_{ad}$ of CO$_2$ was positive, which means that CO$_2$ molecule cannot be adsorbed on the surface of calcium carbonate. Therefore, the adsorption of CO$_2$ is not discussed in the following.

Since the percentage of CH$_4$ is dominant in shale gas, the adsorption energy of CH$_4$ was compared for different adsorption sites to analyze the stability of shale gas molecules adsorbed on CaCO$_3$ (100) surfaces, as shown in Figure 5. It can be seen that CH$_4$ molecules had the lowest $\Delta E_{ad}$ at the H3 site.

From the point of view of the quantity of adsorption energy, CH$_4$ molecules had a minimum adsorption energy of -0.4160 eV at H3, which was the most stable adsorption structure among the 12 high-symmetry sites (Fig. 6). Therefore, it is relatively easier for CH$_4$ molecules to be adsorbed on H3. When adsorbed on T2, CH$_4$ molecules had a maximum energy of -0.3625 eV, which means that it was most difficult for T2 to adsorb CH$_4$ molecules. Similarly, C$_2$H$_6$ molecules had their minimum adsorption energy and most stable adsorption structure at B14, which was the position for easiest adsorption. B24 had the maximum energy and the most unstable adsorption structure. At T2, N$_2$ molecules had their minimum adsorption energy, and could be easily adsorbed at T2. B21 was the most difficult position to adsorb N$_2$ molecules. The small absolute values of adsorption energy indicate very weak adsorption of CH$_4$, C$_2$H$_6$ and N$_2$ molecules on CaCO$_3$ (100) surfaces.

In terms of the range of adsorption energies, the adsorption energy of CH$_4$ at different sites ranged from -0.3625 eV to -0.4160 eV, with the largest difference being only 0.0535 eV. Besides, the largest differences of the adsorption energy ranges for C$_2$H$_6$ and N$_2$ molecules were only 0.1177 eV and 0.0762 eV, respectively. The range of adsorption energies was very small, which indicates that the adsorption of each gas molecule at the high-symmetry sites on CaCO$_3$ (100) surfaces was very similar, and the gas molecules tended to move on the calcium carbonate surfaces. By comparison, it is known that the mobility of CH$_4$ is the strongest.

Analysis of physical structure

In Table II, we can see that after CH$_4$ molecules were adsorbed at H3 sites, the C-H bond length became 0.1097 nm, which is in good agreement with the experimentally spectroscopic data of 0.1086 ± 0.0001 nm (38). Compared with the value before adsorption, the bond length changed by 0.091%, and bond angle changed by 0.779%.

Similarly, the physical structure was analyzed for C$_2$H$_6$ and N$_2$ before and after adsorption. The relative changes were 1.422% and 1.400% for C=C bond length and H-C-H bond angle of C$_2$H$_6$, respectively. The N≡N bond length increased by 1.396% after N$_2$ was adsorbed. It was found that the structures of CH$_4$, C$_2$H$_6$ and N$_2$ molecules showed negligible changes, so the adsorption effect was weak on the CaCO$_3$ (100) surface.

Analysis of density of states

The CASTEP module can analyze the band structure, electronic density of states (DOS), optical properties, phonon dispersion relations, phonon DOS and stress before and after the optimization of the physical model. Here we mainly discuss the electronic DOS changes and their effect on adsorption. According to the analysis of the DOS changes for CH$_4$, C$_2$H$_6$, N$_2$ and CaCO$_3$ (100) surfaces before and after adsorption, the interactions between shale gas molecules and CaCO$_3$ (100) surface can be further understood.
In Figure 7, the DOS of CH4 before and after adsorption at H3 and T2 is compared. The black curve represents the electronic DOS before adsorption, the red curve represents the electronic DOS after adsorption at H3, and the blue curve represents the electronic DOS after adsorption at T2. The vertical dashed line at 0 eV indicates the Fermi level. It can be seen that whether adsorbed at H3 or T2, the electron DOS curves of CH4 molecules shifted to the left overall after adsorption. The adsorption energy decreased, and the electronic structure became more stable, which shows that the adsorption had a significant influence on the distribution of electron DOS of CH4 molecules. Besides, the DOS curve of H3 has 2 peaks, at -12.77 eV and -5.18 eV, which move to the left about 0.3 eV compared with those of T2 at -12.47 eV and -4.88 eV. It is thus proven that the adsorption of CH4 molecules on CaCO3 surfaces at high-symmetry sites is basically from the point of view of electronic structure, and has better mobility on the surface of the calcium carbonate.

Figure 8 shows the partial density of states (PDOS) of oxygen atoms in CaCO3(100) surface before and after the adsorption of CH4 at H3 site and T2 site. The black dotted line indicates the Fermi level.

Figure 9 presents the DOS of CH4, C2H6, and N2 adsorbed on a CaCO3(100) surface. We can see that the adsorption of different gas molecules on the CaCO3(100) surface has similar effects on the electronic structure of the oxygen atom on the CaCO3(100) surface. After adsorption, the 3 DOS curves almost overlap, indicating that CH4, C2H6, and N2 molecules have similar adsorption effects on oxygen atoms on the CaCO3(100) surface to those of the CH4 molecule, and the adsorption of the 3 kinds of gas molecules on the CaCO3(100) surface are physical.

| Gas type | Before adsorption | After adsorption* | Relative change |
|----------|------------------|------------------|-----------------|
|          | Bond length† (nm) | Bond angle‡ (°)  | Bond length (nm) | Bond angle (°) | Bond length | Bond angle |
| CH4      | 0.1098 109.483    | 0.1097 110.336   | 0.091% 0.779%    |
| C2H6     | 0.1547 109.471    | 0.1525 107.938   | 1.422% 1.400%    |
| N2       | 0.1146 180        | 0.1162 180       | 1.396% 0%         |

* Situation for the most stable adsorption position.
† The bond lengths were C-H for CH4, C = C for C2H6, N = N for N2.
‡ The bond angles were C-H for CH4 and C2H6, N = N for N2.
Using the first-principle method based on DFT, we established adsorption models for CH$_4$, C$_2$H$_6$, CO$_2$ and N$_2$ on CaCO$_3$ (100) surfaces, and calculated the corresponding adsorption energies. The adsorption abilities of CH$_4$, C$_2$H$_6$ and N$_2$ molecules on the CaCO$_3$ (100) surface were weak. CO$_2$ molecules could not be adsorbed. The adsorption abilities of the different molecules were different. The adsorption ability of hydrocarbon gas was stronger than that of nonhydrocarbon gas, and the adsorption ability of C$_2$H$_6$ was stronger than that of CH$_4$. In addition, the adsorption energy of different gas molecules varied over the range of sites and followed the order of CH$_4$ < N$_2$ < C$_2$H$_6$. The change of CH$_4$ was the smallest, indicating the best mobility of CH$_4$ molecules on the surface of calcium carbonate. This may be due to the fact that the methane molecule has the smallest relative molecular mass.

We also analyzed the electronic structures of the adsorption systems. After adsorption, the changes of geometric structures of the molecules were small and the electron DOS of atoms in the CaCO$_3$ (100) surface was basically unchanged. The findings above show that the adsorption of shale gas molecules on the surface of calcium carbonate is physical.

Acknowledgements

The authors would like to acknowledge the assistance of A.P. Li P. Chen for English correction.

Fig. 8 - Partial density of states (PDOS) and density of states (DOS) of oxygen atoms in CaCO$_3$ (100) surface before and after the adsorption of CH$_4$ molecules on the H3 site. (A) Before adsorption and (B) after adsorption.

Fig. 9 - Density of states (DOS) of oxygen atoms on CaCO$_3$ (100) surface after the adsorption of CH$_4$, C$_2$H$_6$, and N$_2$ molecules at the most stable adsorption sites.

Conclusions

Disclosures

Financial support: This work was supported by the Young Scientists Fund of the National Natural Science Foundation of China (grant no. S1204141), the Major Program of the National Natural Science Foundation of China (grant no. S1374179), the Southwest Petroleum University Foundation (grant no. 2014QHJ009, 2015JYJ-07) and the Open Research Fund of the Computational Physics Key Laboratory of Sichuan Province (grant no. JSWL2014KF03). Conflict of interest: The authors declare they have no conflicts of interest.

References

1. Kong DT, Ning ZF, Yang F, He B, Zhao TY. The characteristic of adsorption on shales and influence factor. Petrochem Ind Appl. 2013;32(9):1-4.
2. Ma YL, Zhang DL. Research status of shale reservoir adsorption mechanism and its influencing factors. Ground Water. 2014;36(6):246-249.
3. Gao LF, Wang QQ, Yin S, Zheng LH, Wang YY, Li H. Research of shale gas’ adsorption. Sichuan Univ Arts Sci J. 2014;24(2):60-64.
4. Zeng QS, Chen WK, Dai WX, Zhang YF, Li Y, Guo X. Density functional theory study of CO and O$_2$ adsorption on NiFeB$_2$/TiO$_2$ surface. Chin J Catal. 2010;31(4):423-428.
5. Ji LM, Qiu JL, Zhang TW, Xia YQ. Experiments on methane adsorption of common clay minerals in shale. Earth Sci J Chin Univ Geosci. 2012;37(5):1043-1050.
18. Kuang XJ, Wang XQ, Liu GB. A density functional theory study of methane adsorption on Ni(110). J Inner Mongolia Norm Univ. 2015;44(3):389-395.

19. Luo Q, Tang B, Zhang Z, Ran ZL. First principles calculation of adsorption of H2S on Fe(100) surface. Acta Phys Sin. 2013;62(7):077101.

20. Luo XP, Wu P, Zhao JH, Yang N. Study advances on organic pores in organic matter-rich mud shale. J Chengdu Univ Technol. 2015;42(1):50-59.

21. Brunsvold AL, Garton DJ, Minton TK, Troya D, Schatz GC. Crossed beams and theoretical studies of the dynamics of heterothermal collisions between Ar and ethane. J Chem Phys. 2004;121(23):11702-11714.

22. Nave S, Tiwari AK, Jackson B. Methane dissociation and adsorption on Ni(111), Pt(111), Ni(100). Pt(100), and Pt(110)- (1 × 2); energetic study. J Chem Phys. 2010;132(5):054705.

23. Li P, Liu ZZ, Liu GX, Liu DS, Ge XW. Density functional theory study of methane adsorption on Ni(110). J Inner Mongolia Norm Univ. 2015;44(3):389-395.

24. Atta-Fynn R, Ray AK. A first principles study of the adsorption and dissociation of CO on the δ–Pu (111) surface. Eur Phys J B. 2009;70(2):171-184.

25. Li L, Cockayne E, Williamson I, Espinal L, Wong-Ng W. First-principles studies of carbon dioxide adsorption in cryptomelane/hollandite-type manganese dioxide. Chem Phys Lett. 2013;580:120-125.

26. Jiao Y, Du AJ, Zhu ZH, Rudolph V, Simth SC. Adsorption of carbon dioxide and nitrogen on single-layer aluminum nitride nanostructures studied by density functional theory. J Phys Chem C. 2010;114(17):7846-7849.

27. Bevilacqua RC, Rigo VA, Verissimo-Alves M, Miranda CR. NMR characterization of hydrocarbon adsorption on calcite surfaces: a first principles study. J Chem Phys. 2014;141(20):204705.

28. Hohenberg P, Kohn W. Inhomogeneous electron gas. Phys Rev. 1964;136(12):1133-1138.

29. Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett. 1996;77(18):3865-3868.

30. Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. Phys Rev B. 1976;13(12):5188-5192.

31. Monkhorst PK, Jepsen S. A new approach to variable metric algorithms. Comput J. 1970;13(3):317-322.

32. Fletcher R. A modified variable metric method for minimum computation of functions. Comput J. 1970;13(3):317-322.

33. Goldfarb D. A family of variable metric methods derived by variational means. Math Comput. 1970;24(109):23-26.

34. Shanno DF. Conditioning of quasi-Newton methods for function minimization. Math Comput. 1970;24(111):647-656.

35. Graf DL. Crystallographic tables for the rhombohedral carbonates. Am Mineral. 1961;46(11):1283-1316.

36. Zhang H, Liu SY, Zhang CY, eds. Landscape painting the chemistry of quantum mechanics. Beijing, China: Science Press; 2004;215-217.

37. Atta-Fynn R, Ray AK. A first principles study of the adsorption and dissociation of CO on the δ–Pu (111) surface. Eur Phys J B. 2009;70(2):171-184.

38. Nave S, Tiwari AK, Jackson B. Methane dissociation and adsorption on Ni(111), Pt(111), Ni(100). Pt(100), and Pt(110)- (1 × 2); energetic study. J Chem Phys. 2010;132(5):054705.

39. Atta-Fynn R, Ray AK. A first principles study of the adsorption and dissociation of CO on the δ–Pu (111) surface. Eur Phys J B. 2009;70(2):171-184.

40. Nave S, Tiwari AK, Jackson B. Methane dissociation and adsorption on Ni(111), Pt(111), Ni(100). Pt(100), and Pt(110)- (1 × 2); energetic study. J Chem Phys. 2010;132(5):054705.

41. Atta-Fynn R, Ray AK. A first principles study of the adsorption and dissociation of CO on the δ–Pu (111) surface. Eur Phys J B. 2009;70(2):171-184.

42. Nave S, Tiwari AK, Jackson B. Methane dissociation and adsorption on Ni(111), Pt(111), Ni(100). Pt(100), and Pt(110)- (1 × 2); energetic study. J Chem Phys. 2010;132(5):054705.

43. Atta-Fynn R, Ray AK. A first principles study of the adsorption and dissociation of CO on the δ–Pu (111) surface. Eur Phys J B. 2009;70(2):171-184.

44. Nave S, Tiwari AK, Jackson B. Methane dissociation and adsorption on Ni(111), Pt(111), Ni(100). Pt(100), and Pt(110)- (1 × 2); energetic study. J Chem Phys. 2010;132(5):054705.