The study of adsorption of monomolecular water layer on the calcium carbonate methods of the density functional theory

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Abstract
A mechanism is investigated in this paper. geometric and energy characteristics of the process of moisture sorption on the calcite surface (110), which is one of the most widespread crystalline modifications of calcium carbonate, in particular being the main constituent of such a mineral as chalk.

Calculations of a cluster $(CaCO_3)_{20}$ with a fixed structure corresponding to the crystal structure of calcite and having a developed surface of the (110) type are calculated. The surface area (110) was 147.5 $Å^2$.

Sorption of 5 and 6 water molecules on a cluster $(CaCO_3)_{20}$ was studied. The geometry of the cluster was fixed, the position of the water molecules was optimized.

The following calculation methods were used: semi-empirical PM7 method for primary calculations, pure DFT methods with PBE functional for calculating system geometry, DFT with B3LYP5 hybrid functional and 6-31G (d, p) full-electron basis for calculating the geometry and energy of the system. When calculating the adsorption energy, the BSSE correction was taken into account.

The accuracy of calculating the geometry of the system for fast methods (semi-empirical PM7 and pure DFT methods with different bases) is compared with DFT/B3LYP5/6-31G(d,p).

As a result of the study, the configuration of the active centers of the calcite surface (110), involved in the adsorption of water molecules and the energy of water sorption for various configurations of interaction with the active center, was determined.

References
[1] S.I. Niftaliev, Yu.S. Peregudov, Yu.G. Podrezova. Effect of the mass fraction of a hydrophobic and ferromagnetic agent on the sorption characteristics of calcium carbonate. *Sorption and chromatographic processes.* **2013**. Vol.13. P.338-343. (russian)
[2] A.A. Komissarenkov, V.G. Khorkov. Modification of chalk NPAA for use as an additive in the process of degreasing of waste paper during the dissolution. *Forest Journal.* **2009**. No6. P.119-124. (russian)
[3] V.V. Nazarova. Intensification of the process of production of fine chalk for composite materials. Abstract. *Belgorod: BSTU them. V.G. Shukhov.* **2012**. P.19. (russian)
[4] O.H. Poleshchuk, E.G. Fateev, S.V. Kovalev. The analysis of the interaction of metallic mercury with ammonium bases on the basis of the density functional theory. *Butlerov Communications.* **2012**. Vol.32. No.12. P.149-154. ROI: jbc-02/12-32-12-149
[5] T.I. Izaak, D.O. Martynova, O.H. Poleshchuk. The analysis of the interaction between the four nuclear cluster of silver to the surface of the silicon dioxide methods of the density functional theory. *Butlerov Communications.* **2013**. Vol.36. No.11. P.22-29. ROI: jbc-02/13-36-11-22
[6] A.A. Doroshenko, I.V. Nechaev, A.V. Vvedensky. Quantum-chemical мodeling of the hydroxide ion gas-phase adsorption on IB metal clusters Men (n = 2-8). *Butlerov Communications.* **2015**. Vol.41. No.2. P.135-140. DOI: 10.37952/ROI-jbc-01/15-41-2-135
[7] A.A. Degtyarev, A.G. Tarakanov. Comparison of methods for the study of water sorption on the titanium oxide. *Butlerov Communications.* **2017**. Vol.50. No.4. P.105-111. DOI: 10.37952/ROI-jbc-01/17-50-4-105

[8]   M. Prencipe, F. Pascale, C.M. Zicovich-Wilson, V.R. Saunders, R. Orlando, R. Dovesi. The vibrational spectrum of calcite (CaCO₃): an ab initio quantum-mechanical calculatio. *Phys Chem Minerals*. **2004**. Vol.31. P.559-564.

[9]   C.G. Ungureanu, M. Prencipe, R. Cossio. Ab initio quantum-mechanical calculation of CaCO₃ aragonite at high pressure: thermodynamic properties and comparison with experimental data. *Eur. J. Mineral*. **2010**. Vol.22. P.693-701.

[10] V.A. Poluektova, N.A. Shapovalov, L.N. Balyatinskaya. Adsorption of oxyphenol furfural oligomers on dispersed materials. *Technical science*. **2012**. No.11. P.1470-1474. (russian)

[11] Ch. Santschi, M. J. Rossi Uptake of CO₂, SO₂, HNO₃ and HCl on Calcite (CaCO₃) at 300 K: Mechanism and the Role of Adsorbed Water. *J. Phys. Chem*. **2006**. Vol.110. P.6789-6802.

[12] E.N. Maslem, V.A. Streltsov, N.R. Streltsova X-ray study of electron density in calcite. *Acta Crystallogr*. **1993**. Vol.49. P.636-641.

[13] J.J.P. Stewart Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters. *J. Mol. Modeling*. **2013**. Vol.19. P.1-32.

[14] Mopac2012 Home Hage [Electronic resource]: What is MOPAC2016. URL: http://openmopac.net/MOPAC2016.html (access date: 11.05.**2017**).

[15] L. Chengteh, Y. Weitao, P. Robert Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev*. **1988**. B.37. P.785-789.

[16] P.C. Hariharan, J.A. Pople. *Theoret. Chimica Acta*. **1973**. Vol.28. P.213-222.

[17] V.A. Rassolov, J.A. Pople, M.A. Ratner, T.L. Windus. *J. Chem. Phys*. **1998**. Vol.109. P.1223-1229.

[18] Alex A. Granovsky, Firefly version 8 [Electronic resource]: Introduction to the Firefly. URL: http://classic.chem.msu.su/gran/gamess/index.html (access date: 16.05.**2017**).

[19] D.N. Laikov. Fast evaluation of density functional exchange-correlation terms using the expansion of the electron density in auxiliary basis sets. *Chem. Phys. Lett*. **1997**. Vol.281. P.151-156.

[20] J.P. Perdew, K. Burke, M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett*. **1996**. Vol.77. P.3865.

[21] D.N. Laikov. A new class of atomic basis functions for accurate electronic structure calculations of molecules. *Chem. Phys. Lett*. **2005**. Vol.416. P.116-120.

[22] S.F. Boys, F. Bernardi. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol. Phys*. **1970**. Vol.19. P.553-566.

[23] I. Mayer. *J.Comput. Chem*. **2007**. Vol.28. P.204-221.

[24] N.A. Korovina. Course of General Chemistry. Ed. N.V. Korovin. *Moscow High School*. **1990**. P.446. (russian)

[25] V.V. Voevodin, S.A. Zhumatiy, S.I. Sobolev, A.S. Antonov, P.A. Bryzgalov, D.A. Nikitenko, K.S. Stefanov. Practice of «Lomonosov» Supercomputer. Open Systems J. Moscow. *Open Systems Publ*. **2012**. No.7. P.36-39. (russian)