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ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ КИНЕТИКИ ДИМЕРИЗАЦИИ ОКСИДА АЛЮМИНИЯ*

А.С. Шарипов[1], Б. И. Луховицкий[2]

Аннотация: Исследована реакция димеризации оксида алюминия методами квантовой химии. С помощью гибридного функционала электронной плотности с коррекцией по теории возмущений второго порядка B2PLYP построена соответствующая поверхность потенциальной энергии (ППЭ). Показано, что взаимодействие двух мономеров Al_2O_3 даже в простейшем случае приводит к образованию димеров $(Al_2O_3)_2$ в различных изомерных формах. Анализ, основанный на теории Райса–Рамспергера–Касселя–Маркуса (PPKM), показал, что константа скорости процесса димеризации $2Al_2O_3 \rightarrow (Al_2O_3)_2$ может быть на порядки ниже, чем оценка по модели твердых сфер. Зависимость соответствующей константы скорости от температуры и давления в диапазонах $T = 300$–3000 K и $P = 10^{-4}$–10^2 атм может быть представлена в форме Линдемана следующим образом: $k_0(T) = 8{,}01 \cdot 10^{19} T^{-1{,}079} \exp(21671/T)$ см^6/(моль^{2}с); $k_\infty(T) = 9{,}91 \cdot 10^{19} T^{-1{,}754} \exp(-2911/T)$ см^3/(моль·с).

Ключевые слова: оксид алюминия; димеризация; PPKM

Литература

1. *Catlow C. R. A., Bromley S. T., Hamad S., Mora-Fonz M., Sokol A. A., Woodley S. M.* Modelling nano-clusters and nucleation // Phys. Chem. Chem. Phys., 2010. Vol. 12. P. 786–811.
2. *Lam J., Amans D., Dujardin C., Ledoux G., Allouche A. R.* Atomistic mechanisms for the nucleation of aluminium oxide nanoparticles // J. Phys. Chem. A, 2015. Vol. 119. P. 8944–8949.
3. *Girshick S. L., Agarwal P., Truhlar D. G.* Homogeneous nucleation with magic numbers: Aluminum // J. Chem. Phys., 2009. Vol. 131. P. 134305.
4. *Kathmann S. M., Schenter G., Garrett B. C., Chen B., Siepmann J. I.* Thermodynamics and kinetics of nanoclusters controlling gas-to-particle nucleation // J. Phys. Chem. C, 2009. Vol. 113. P. 10354–10370.
5. *Kashchiev, D.* Nucleation: Basic theory with applications. — Oxford: Butterworth-Heinemann, 2000. 549 p.
6. *Bykov N. Y., Gorbachev Y. E.* Mathematical models of water nucleation process for the Direct Simulation Monte Carlo method // Appl. Math. Comput., 2017. Vol. 296. P. 215–232.
7. *Savel'ev A. M., Starik A. M.* An improved model of homogeneous nucleation for high supersaturation conditions: Aluminum vapor // Phys. Chem. Chem. Phys., 2017. Vol. 19. P. 523–538.
8. *Kozasa T., Hasegawa H.* Grain formation through nucleation process in astrophysical environments. II. Nucleation and grain growth accompanied by chemical reaction // Prog. Theor. Phys., 1987. Vol. 77. P. 1402–1410.
9. *Nittler L. R., Alexander C. M. O'D., Gao X., Walker R. M., Zinner E.* Stellar sapphires: The properties and origins of presolar Al_2O_3 in meteorites // Astrophys. J., 1997. Vol. 483. No. 1. P. 475–495.
10. *Dörre E., Hübner H.* Alumina: Processing, properties, and applications. — Materials research and engineering ser. — Berlin–Heidelberg: Springer-Verlag, 1984. 444 p.
11. *Henrich V. E., Cox P. A.* The surface science of metal oxides. — Cambridge: Cambridge University Press, 1994. 478 p.
12. *Fernandez E., Eglitis R. I., Borstel G., Balbas L. C. Ab initio* calculations of H_2O and O_2 adsorption on Al_2O_3 substrates // Comput. Mater. Sci., 2007. Vol. 39. P. 587–592.
13. *Karasev V. V., Onischuk A. A., Glotov O. G., Baklanov A. M., Maryasov A. G., Zarko V. E., Panfilov V. N., Levykin A. I., Sabelfeld K. K.* Formation of charged aggregates of Al_2O_3 nanoparticles by combustion of aluminum droplets in air // Combust. Flame, 2004. Vol. 138. P. 40–54.
14. *Бекстед М. В., Лианг У., Паддуппакам К. В.* Математическое моделирование горения одиночной алюминиевой частицы // Физика горения и взрыва, 2005. № 41. С. 15–33.
15. *Старик А. М., Савельев А. М., Титова Н. С.* Особенности воспламенения и горения композитных топлив, содержащих наночастицы алюминия (обзор) // Физика горения и взрыва, 2015. № 51. С. 64–91.
16. *Nemukhin A. V., Weinhold F.* Structures of the aluminum oxides studied by ab initio methods with natural bond orbital analysis // J. Chem. Phys., 1992. Vol. 97. P. 3420–3430.
17. *Chang C., Patzer A. B. C., Sedlmayr E., Sulzle D. Ab initio* studies of stationary points of the Al_2O_3 molecule // Eur. Phys. J. D, 1998. Vol. 2. P. 57–62.

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[1]Центральный институт авиационного моторостроения им. П. И. Баранова, sharipov@ciam.ru
[2]Центральный институт авиационного моторостроения им. П. И. Баранова, loukhovitski@ciam.ru

18. *Archibong E. F., St-Amant A.* On the structure of Al_2O_3 and photoelectron spectra of $Al_2O_2^-$ and $Al_2O_3^-$ // J. Phys. Chem. A, 1999. Vol. 103. No. 8. P. 1109–1114.
19. *Шарипов А. С., Ведищев И. Ю.* Исследование стехиометрических кластеров оксида алюминия методами квантовой химии // Тр. 54-й научн. конф. МФТИ: Аэромеханика и летательная техника, 2011. С. 17–19.
20. *Mitin A. V.* Accurate theoretical IR and Raman spectrum of Al_2O_2 and Al_2O_3 molecules // Struct. Chem., 2011. Vol. 22. P. 411–418.
21. *Rahane A. B., Deshpande M. D., Kumar V.* Structural and electronic properties of $(Al_2O_3)_n$ clusters with $n = 1–10$ from first principles calculations // J. Phys. Chem. C, 2011. Vol. 115. P. 18111–18121.
22. *Woodley S. M.* Atomistic and electronic structure of $(X_2O_3)_n$ nanoclusters; $n = 1–5$, X = B, Al, Ga, In and Tl // Proc. R. Soc. A, 2011. Vol. 467. P. 2020–2042.
23. *Sharipov A. S., Loukhovitski B. I., Starik A. M.* Theoretical study of structure and physical properties of $(Al_2O_3)_n$ clusters // Phys. Scr., 2013. Vol. 88. P. 058307. 10 p.
24. *Поскребышев Г. А., Ермаков А. Н.* Определение значений $\Delta_f H^0_{298}$ для Al_2O_3 и его кластеров $(Al_2O_3)_n$ с $n = 2$ и 4 // Горение и взрыв, 2017. Т. 10. №4. С. 45–50.
25. *Schwabe T., Grimme S.* Double-hybrid density functionals with long-range dispersion corrections: Higher accuracy and extended applicability // Phys. Chem. Chem. Phys., 2007. Vol. 9. P. 3397–3406.
26. *Grimme S.* Semiempirical hybrid density functional with perturbative second-order correlation // J. Chem. Phys., 2006. Vol. 124. P. 034108. 16 p.
27. *Zhang I. Y., Xu X.* Doubly hybrid density functional for accurate description of thermochemistry, thermochemical kinetics and nonbonded interactions // Int. Rev. Phys. Chem., 2011. Vol. 30. P. 115–160.
28. *Bousquet D. Bremond E., Sancho-Garcia J. C., Ciofini I., Adamo C.* Is there still room for parameter free double hybrids? Performances of PBE0-DH and B2PLYP over extended benchmark sets // J. Chem. Theory Comput., 2013. Vol. 9. P. 3444–3452.
29. *Sharipov A. S., Starik A. M.* Theoretical study of the reactions of ethanol with aluminum and aluminum oxide // J. Phys. Chem. A, 2015. Vol. 119. P. 3897–3904.
30. *Sharipov A. S., Starik A. M.* Quantum chemical study of the reactions of Al, AlO and AlOH with H_2O_2 // Chem. Phys., 2016. Vol. 465-466. P. 9–16.
31. *Kendall R. A., Dunning T. H., Jr., Harrison R. J.* Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions // J. Chem. Phys., 1992. Vol. 96. P. 6796–6806.
32. *Granovsky A. A.* Firefly V. 8.0. http://classic.chem.msu.su/gran/firefly/index.html.
33. *Fernandez-Ramos A., Miller J. A., Klippenstein S. J., Truhlar D. G.* Modeling the kinetics of bimolecular reactions // Chem. Rev., 2006. Vol. 106. P. 4518–4584.
34. *Knyazev, V. D., Tsang W.* Chemically and thermally activated decomposition of secondary butyl radical // J. Phys. Chem. A, 2000. Vol. 104. P. 10747–10765.
35. *Mokrushin V., Bedanov V., Tsang W., Zachariah M., Knyazev V., McGivern W. S.* ChemRate, version 1.5.10. 2011. http://kinetics.nist.gov/ChemRate.
36. *Burcat A., Ruscic B.* Third millennium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables. ANL-05/20 and TAE 960. Aerospace Engineering, and Argonne National Laboratory, Chemistry Division: Technion-IIT, 2005.
37. *Catoire L., Legendre J. F., Giraud M.* Kinetic model for aluminum-sensitized ram accelerator combustion // J. Propul. Power, 2003. Vol. 19. P. 196–202.
38. *Sharipov A. S., Loukhovitski B. I., Tsai C.-J., Starik A. M.* Theoretical evaluation of diffusion coefficients of $(Al_2O_3)_n$ clusters in different bath gases // Eur. Phys. J. D, 2014. Vol. 68. P. 99.
39. *Ning N., Couedel L., Arnas C., Khrapak S.* Computational prediction of rate constant for reactions involved in Al clustering // J. Phys. Chem. A, 2017. Vol. 121. P. 8333–8340.
40. *Zachariah M. R., Tsang W.* Theoretical prediction of gas-phase nucleation kinetics of SiO // MRS Online Proceedings Library Archive, 1993. Vol. 334. P. 19–24.
41. *Schenter G. K., Kathmann S. M., Garrett B. C.* Variational transition state theory of vapor phase nucleation // J. Chem. Phys., 1999. Vol. 110. P. 7951–7959.
42. *Baulch D. L., Bowman C. T., Cobos C. J., et al.* Evaluated kinetic data for combustion modeling // J. Phys. Chem. Ref. Data, 2005. Vol. 34. P. 757–1397.

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THEORETICAL STUDY OF DIMERIZATION KINETICS OF ALUMINUM OXIDE

A. S. Sharipov and B. I. Loukhovitski

Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow, 111116 Russian Federation

Abstract: The study is aimed at the quantum chemical investigation of alumina dimerization. The appropriate potential energy surface is explored using the hybrid density functional with perturbative second-order correlation B2PLYP. It is shown that the interaction of two Al_2O_3 monomers leads to $(Al_2O_3)_2$ formation in different forms. The RRKM-based analysis revealed that the rate constant of $2Al_2O_3 \rightarrow (Al_2O_3)_2$ process can be lower by several orders of magnitude than the estimates by the rigid-sphere theory. The corresponding temperature- and pressure-dependent rate constant can be expressed by the Lindemann fit as follows: $k_0(T) = 8.01 \cdot 10^{19} T^{-1.079} \exp(21671/T)$ cm^6/(mole^{2}s) and $k_\infty(T) = 9.91 \cdot 10^{19} T^{-1.754} \exp(-2911/T)$ cm^3/(mole·s).

Keywords: alumina; dimerization; RRKM

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References

1. Catlow, C. R. A., S. T. Bromley, S. Hamad, M. Mora-Fonz, A. A. Sokol, and S. M. Woodley. 2010. Modelling nano-clusters and nucleation. *Phys. Chem. Chem. Phys.* 12:786–811.
2. Lam, J., D. Amans, C. Dujardin, G. Ledoux, and A. R. Allouche. 2015. Atomistic mechanisms for the nucleation of aluminium oxide nanoparticles. *J. Phys. Chem. A* 119:8944–8949.
3. Girshick, S. L., P. Agarwal, and D. G. Truhlar. 2009. Homogeneous nucleation with magic numbers: Aluminum. *J. Chem. Phys.* 131:134305.
4. Kathmann, S. M., G. Schenter, B. C. Garrett, B. Chen, and J. I. Siepmann. 2009. Thermodynamics and kinetics of nanoclusters controlling gas-to-particle nucleation. *J. Phys. Chem. C* 113:10354–10370.
5. Kashchiev, D. 2000. *Nucleation: Basic theory with applications*. Oxford: Butterworth-Heinemann. 549 p.
6. Bykov, N. Y., and Y. E. Gorbachev. 2017. Mathematical models of water nucleation process for the Direct Simulation Monte Carlo method. *Appl. Math. Comput.* 296:215–232.
7. Savel'ev, A. M., and A. M. Starik. 2017. An improved model of homogeneous nucleation for high supersaturation conditions: Aluminum vapor. *Phys. Chem. Chem. Phys.* 19:523–538.
8. Kozasa, T., and H. Hasegawa. 1987. Grain formation through nucleation process in astrophysical environments. II. Nucleation and grain growth accompanied by chemical reaction. *Prog. Theor. Phys.* 77:1402–1410.
9. Nittler, L. R., C. M. O'D. Alexander, X. Gao, R. M. Walker, and E. Zinner. 1997. Stellar sapphires: The properties and origins of presolar Al_2O_3 in meteorites. *Astrophys. J.* 483(1):475–495.
10. Dörre, E., and H. Hübner. 1984. *Alumina: Processing, properties, and applications.* Materials research and engineering ser. Berlin–Heidelberg: Springer-Verlag. 444 p.
11. Henrich, V. E., and P. A. Cox. 1994. *The surface science of metal oxides.* Cambridge: Cambridge University Press. 478 p.
12. Fernandez, E., R. I. Eglitis, G. Borstel, and L. C. Balbas. 2007. *Ab initio* calculations of H_2O and O_2 adsorption on Al_2O_3 substrates. *Comput. Mater. Sci.* 39:587–592.
13. Karasev, V. V., A. A. Onischuk, O. G. Glotov, A. M. Baklanov, A. G. Maryasov, V. E. Zarko, V. N. Panfilov, A. I. Levykin, and K. K. Sabelfeld. 2004. Formation of charged aggregates of Al_2O_3 nanoparticles by combustion of aluminum droplets in air. *Combust. Flame* 138:40–54.
14. Beckstead, M. W., Y. Liang, and K. V. Pudduppakkam. 2005. Numerical simulation of single aluminum particle combustion. *Combust. Explo. Shock Waves* 17:622–638.
15. Starik, A. M., A. M. Savel'ev, and N. S. Titova. 2015. Specific features of ignition and combustion of composite fuels containing aluminum nanoparticles (review). *Combust. Explo. Shock Waves* 51:197–222.
16. Nemukhin, A. V., and F. Weinhold. 1992. Structures of the aluminum oxides studied by ab initio methods with natural bond orbital analysis. *J. Chem. Phys.* 97: 3420–3430.
17. Chang, C., A. B. C. Patzer, E. Sedlmayr, and D. Sulzle. 1998. *Ab initio* studies of stationary points of the Al_2O_3 molecule. *Eur. Phys. J. D* 2:57–62.
18. Archibong, E. F., and A. St-Amant. 1999. On the structure of Al_2O_3 and photoelectron spectra of $Al_2O_2^-$ and $Al_2O_3^-$. *J. Phys. Chem. A* 103(8):1109–1114.
19. Sharipov, A. S., and I. Yu. Vedishchev. 2011. Issledovanie stekhiometricheskikh klasterov oksida alyuminiya metodami kvantovoy khimii [Quantum chemistry study of stoichiometric alumina clusters]. *Tr. 54-y nauchn. konf.*

MFTI, Aeromekhanika i letatel'naya tekhnika [54th Scientific Conference of MIPT: Aeromechanics and Flight Engineering Proceedings]. 17–19.

20. Mitin, A. V. 2011. Accurate theoretical IR and Raman spectrum of Al_2O_2 and Al_2O_3 molecules. *Struct. Chem.* 22:411–418.
21. Rahane, A. B., M. D. Deshpande, and V. Kumar. 2011. Structural and electronic properties of $(Al_2O_3)_n$ clusters with $n = 1$–10 from first principles calculations. *J. Phys. Chem. C* 115:18111–18121.
22. Woodley, S. M. 2011. Atomistic and electronic structure of $(X_2O_3)_n$ nanoclusters; $n = 1$–5, X = B, Al, Ga, In and Tl. *Proc. R. Soc. A* 467:2020–2042.
23. Sharipov, A. S., B. I. Loukhovitski, and A. M. Starik. 2013. Theoretical study of structure and physical properties of $(Al_2O_3)_n$ clusters. *Phys. Scr.* 88:058307. 10 p.
24. Poskrebyshev, G. A., and A. N. Ermakov. 2017. Opredelenie znacheniy $\Delta_f H^0_{298,15}$ dlya Al_2O_3 i ego klasterov $(Al_2O_3)_n$ s $n = 2$ i 4 [Determination of the values of $\Delta_f H^0_{298.15}$ of Al_2O_3 and its clusters ($(Al_2O_3)_n$) with $n = 2$ and 4]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 10(4):45–50.
25. Schwabe, T., and S. Grimme. 2007. Double-hybrid density functionals with long-range dispersion corrections: Higher accuracy and extended applicability. *Phys. Chem. Chem. Phys.* 9:3397–3406.
26. Grimme, S. 2006. Semiempirical hybrid density functional with perturbative second-order correlation. *J. Chem. Phys.* 124:034108. 16 p.
27. Zhang, I. Y., and X. Xu. 2011. Doubly hybrid density functional for accurate description of thermochemistry, thermochemical kinetics and nonbonded interactions. *Int. Rev. Phys. Chem.* 30:115–160.
28. Bousquet, D., E. Bremond, J. C. Sancho-Garcia, I. Ciofini, and C. Adamo. 2013. Is there still room for parameter free double hybrids? Performances of PBE0-DH and B2PLYP over extended benchmark sets. *J. Chem. Theory Comput.* 9:3444–3452.
29. Sharipov, A. S., and A. M. Starik. 2015. Theoretical study of the reactions of ethanol with aluminum and aluminum oxide. *J. Phys. Chem. A* 119:3897–3904.
30. Sharipov, A. S., and A. M. Starik. 2016. Quantum chemical study of the reactions of Al, AlO and AlOH with H_2O_2. *Chem. Phys.* 465-466:9–16.
31. Kendall, R. A., T. H. Dunning, Jr., and R. J. Harrison. 1992. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* 96:6796–6806.
32. Granovsky, A. A. Firefly V. 8.0. Available at: http://classic.chem.msu.su/gran/firefly/index.html (accessed January 23, 2018).
33. Fernandez-Ramos, A., J. A. Miller, S. J. Klippenstein, and D. G. Truhlar. 2006. Modeling the kinetics of bimolecular reactions. *Chem. Rev.* 106:4518–4584.
34. Knyazev, V. D., and W. Tsang. 2000. Chemically and thermally activated decomposition of secondary butyl radical. *J. Phys. Chem. A* 104:10747–10765.
35. Mokrushin, V., V. Bedanov, W. Tsang, M. Zachariah, V. Knyazev, and W. S. McGivern. 2011. ChemRate, version 1.5.10 Available at: http://kinetics.nist.gov/ ChemRate (accessed January 23, 2018).
36. Burcat, A., and B. Ruscic. 2005. Third millennium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables. ANL-05/20 and TAE 960. Aerospace Engineering, and Argonne National Laboratory, Chemistry Division: Technion-IIT.
37. Catoire, L., J. F. Legendre, and M. Giraud. 2003. Kinetic model for aluminum-sensitized ram accelerator combustion. *J. Propul. Power* 19:196–202.
38. Sharipov, A. S., B. I. Loukhovitski, C.-J. Tsai, and A. M. Starik. 2014. Theoretical evaluation of diffusion coefficients of $(Al_2O_3)_n$ clusters in different bath gases. *Eur. Phys. J. D* 68:99.
39. Ning, N., L. Couedel, C. Arnas, and S. Khrapak. 2017. Computational prediction of rate constant for reactions involved in Al clustering. *J. Phys. Chem. A* 121:8333–8340.
40. Zachariah, M. R., and W. Tsang. 1993. Theoretical prediction of gas-phase nucleation kinetics of SiO. *MRS Online Proceedings Library Archive* 334:19–24.
41. Schenter, G. K., S. M. Kathmann, and B. C. Garrett. 1999. Variational transition state theory of vapor phase nucleation. *J. Chem. Phys.* 110:7951–7959.
42. Baulch, D. L., C. T. Bowman, C. J. Cobos, *et al.* 2005. Evaluated kinetic data for combustion modeling. *J. Phys. Chem. Ref. Data* 34:757–1397.

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Contributors

Sharipov Alexander S. (b. 1986) — Candidate of Science in physics and mathematics, senior research scientist, Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow 111116, Russian Federation; sharipov@ciam.ru
Loukhovitski Boris I. (b. 1979) — Candidate of Science in physics and mathematics, head of sector, Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow 111116, Russian Federation; loukhovitski@ciam.ru