

Quantum chemical simulation of oxidation of graphite carbon atoms in basal-plane and edge positions

A.G. Grebenyuk¹, D.B. Nasiedkin¹, Yu.V. Plyuto¹

¹ Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine, 17 General Naumov Str., Kyiv 03164, Ukraine.

E-mail: nasiedkindm@gmail.com

Oxidation of natural and synthetic graphites is a subject of long year studies because of standing requirements to improve the safety in the nuclear power industry where they are widely applied. The microstructure of macrocrystalline natural graphite still remains controversial and to a great extent this concerns graphite surface reactivity and its capability to oxidation.

The aim of this work is the quantum chemical simulation of oxidation of graphite carbon atoms in both basal-plane and edge positions resulting in elimination of a carbon atom as CO₂ molecule. The graphite basal plane was simulated by C₄₂H₁₆ cluster model with H-terminated edges (Fig. 1a) using density functional theory (DFT) calculations.

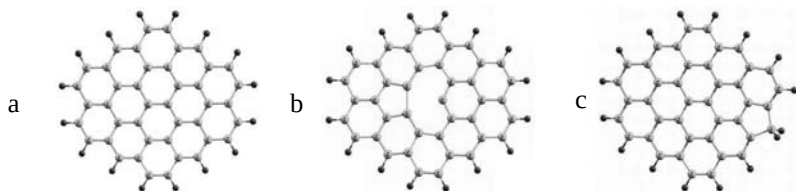


Fig. 1. Optimized structures and total energy values for: a – graphite C₄₂H₁₆ model (-1601.58655 a.u.); b – C₄₁H₁₆ model (-1563.40667 a.u.) after C atom elimination from the basal plane; c – C₄₁H₁₆ model (-1563.64501 a.u.) after C atom elimination from the edge position.

The results of DFT calculation of O₂ molecule interaction with graphite showed that basal plane was energetically unfavourable for elimination of carbon atom as CO₂ molecule since this should result only in the formation of vacancies with altering charge distribution (Fig. 1b). In contrast, the interaction of O₂ molecule with edge carbon atom of graphite sheet can be effective (Fig. 1c). The obtained results agree well with the available experimental data which demonstrate the anisotropy of the natural graphite surface to oxidation. Moreover, the obtained results give us an opportunity to come to the conclusion that defects at graphite basal planes are associated with the original defect sites and cannot be formed as the result of oxidative elimination of carbon atoms.