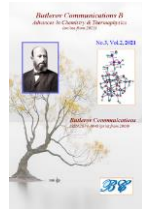
Butlerov Communications B
Advances in Chemistry & Thermophysics
ISSN 2074-0948 (print)

2021. Vol.2, No.3, Id.2.
Journal Homepage: https://b-journal.butlerov.com/

BUTLEROV HERITAGE



Full Paper

Thematic section: Quantum-Chemical Research.
Subsection: Kinetics and Catalysis.

The Reference Object Identifier – ROI-jbc-B/21-2-3-2
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-B/21-2-3-2
Received 16 July 2021; Accepted 19 July 2021

DFT study of propylene glycol dehydrogenation reaction on the smallest cluster of coordination saturated hydroxylated α-form of hematite, corresponding to X-ray diffraction data

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Keywords: DFT method, PBE density functional, hematite, $Fe_{12}H_{18}O_{38}$ cluster, dehydrogenation reaction, propylene glycol, reaction mechanism, supercritical water oxidation.

Abstract

Quantum-chemically, in the approximation of the DFT method and the PBE density functional, the minimum-size cluster of the hydroxylated α-form of hematite ($Fe_{12}O_{20}(OH)_{18}$, more general gross formula: $Fe_{12}H_{18}O_{38}$) is optimized, volume contains all possible cyclic substructures that are important from a chemical point of view. The $Fe_{12}O_{20}(OH)_{18}$ cluster is the smallest, but structurally accurate cluster model of hematite, convenient for quantum chemical research.

During the chemisorption of propylene glycol on the hydroxylated singlet surface of hematite, the formation of hydrogen-bonded pre-reaction complexes is possible. One hydrogen bond is formed between the hydrogen atom at the secondary carbon atom of propylene glycol and the hydroxyl group at the iron atom (hydrogen bond length is 2.03 Å). The second hydrogen bond is formed between the hydroxyl group at the secondary carbon atom of propylene glycol and the bridging oxygen of hematite (the hydrogen bond length is 1.82 Å). Despite the shorter hydrogen bond, in this case we should talk about the stage of chain initiation, in which the primary center of initiation of the reaction is the reaction centers "hydrogen at the secondary carbon atom of propylene glycol - hydroxyl group at the iron atom", since in the transition state only this structural bond undergoes a significant change, increasing the length of the tertiary C–H bond by 1.08 Å and reducing the corresponding hydrogen bond by 0.48 Å. The enthalpy of activation of the forward direction of this

elementary act was symbolic $\Delta H^{\neq}$ = 1.49 kcal/mol, and the enthalpy of activation of the reverse direction $\Delta H^{\neq}\_$ = 52.08 kcal/mol. With such an energetic specificity, this reaction is extremely exothermic and thermodynamically nonequilibrium, that is, irreversible.

Using the example of the reaction of propylene glycol dehydrogenation on the hydroxylated surface of hematite (cluster with the gross formula: $Fe_{12}O_{20}(OH)_{18}$, it was shown that in the case of reactions falling under the definition of the chain initiation stage (this concept was introduced by the authors into scientific practice earlier), multiplet the state of the reaction system does not significantly affect the energy specificity of the processes. This reaction, which occurs with the participation of a water vapor phase under SCF conditions, describes real elementary acts of supercritical water oxidation (SCWO). The primary product of the propylene glycol dehydrogenation reaction on hydroxylated hematite is chemisorbed 1-hydroxypropan-2-one. It can be argued that under these conditions the hematite surface will be represented by a completely hydroxylated form and possible reactions with organic agents should be considered as their interaction with the Fe–O–Fe–O–H structural subgroups of hematite, which are contained in the surface oxide layer of the SCF coil stainless steel the reaction zone, as well as in the iron oxide filling this coil over time as a result of the corrosion process.

For citation: Alexandre I. Kourdioukov, Farid M. Gumerov, Zufar I. Zaripov, Asia R. Gabitova, Almaz U. Aetov, Vladimir G. Uryadov. DFT study of propylene glycol dehydrogenation reaction on the smallest cluster of coordination saturated hydroxylated α-form of hematite, corresponding to X-ray diffraction data. *Butlerov Communications B*. **2021**. Vol.2. No.3. Id.2. DOI: 10.37952/ROI-jbc-B/21-2-3-2

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