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DFT study of elementary acts of supercritical water oxidation by the example of the catalytic reaction of radical water dissociation with the participation of model cluster Fe_4O_6

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Abstract

This report details aspects of the reactivity of the products of catalytic dissociation of water as applied to the description of the nature of supercritical water oxidation and other oxidative SCF processes in general. It has been shown quantum chemically that the products of thermodynamically nonequilibrium to one degree or another dissociation of water on the surface of a model Fe_4O_6 cluster of different multiplet nature can act as effective agents for interaction with atmospheric oxygen and organic compounds. The antiferromagnetic forms of iron oxides can actively participate in radical reactions. It is shown using a model cluster Fe_4O_6 as an example. The radical reactions are able to easily change their multiplet state by simple chemisorption of $^3O_2$ on their surface. In combination with the ability of water to dissociate on the model Fe_4O_6 cluster by the ionic type, the latter can easily transform into a triplet system, which, accordingly, leads to the emergence of an equilibrium biradical water dissociation formally even at room temperature. Hydrate-oxygen interactions on the surface of the Fe_4O_6 cluster lead to the generation of either an extremely reactive iron-hydroperoxide complex or a hydroperoxyl radical capable of conducting oxidative processes under SCF conditions in the volume of the corresponding fluid.

It is shown the dissociative chemisorption of a water molecule on a Fe_4O_6 cluster in a triplet state (initiated, for example, by chemisorption of $^3O_2$), in contrast to the heterolytic dissociation of water (whose thermodynamic equilibrium is shifted towards the molecular form of water), is practically a thermodynamically equilibrium process. It is this fact allowed us to consider the hydride-hydroxyl form of the Fe_4O_6 triplet cluster as one of the real agents for the oxidation of propylene glycol by the example of its first stage of catalytic dehydrogenation.

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