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DFT study of homolytic scission of C–H bonds of alkanes and propylene glycol dehydrogenation reactions on Fe_4O_7, $NiFe_3O_7$ clusters and their protonated and hydroxylated forms

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Abstract

The results of a DFT study of elementary acts, both catalytic transformations of alkanes on hydride-hydroxyl forms of Fe_4O_7 and $NiFe_3O_7$ clusters, and processes of hydrocarbons transformation on iron and nickel-oxide clusters without initially hydride-hydroxyl filling are presented. Homolytic scission of the C–H bonds of alkanes on the hydride-hydroxyl form of the Fe_4O_7 cluster is accompanied by the formation of alkyl radicals capable of biradicals recombination according to the singlet type. There is also an additional reaction direction, which is represented by a singlet intra-associative rearrangement generating alcohols chemisorbed with the iron atom of the Fe_4O_6 cluster. This reaction is irreversible, proceeds with a large exothermic effect of 45.90 kcal·mol^{-1}, sufficient to overcome the chemisorption bond and diffuse into the volume of the supercritical fluid. The calculated characteristics of the interaction of alkanes with an iron-positioned hydroxyl group indicate that the activation energies of the forward direction of elementary acts in the homologous series: primary and secondary C–H bonds, lie in the range of 30.91-32.74 kcal·mol^{-1}, that is, these reactions are not very selective and strongly endothermic, since the activation energies of the reverse directions of the corresponding elementary acts are in the range of 1.40-3.27 kcal·mol^{-1}. The transition in the homologous series from the primary and secondary C–H bonds of propane to the tertiary C–H bonds of isobutane significantly changes the activation specificity of the homolytic scission of C–H bonds. The relative activation energy of the forward direction of the reaction decreases by about 8.00 kcal·mol^{-1}. A reaction system with the participation of the nickel-iron-oxide cluster $NiFe_3O_7$ and propane has been studied quantum-chemically. The result of the interaction of these reagents is the formation of isopropyl alcohol (propan-2-ol), which is chemisorbed with the nickel atom of the $NiFe_3O_6$ cluster. This reaction is irreversible and proceeds with a large exothermic effect of 50.95 kcal·mol^{-1}. The energetics of this process qualitatively coincides with the activation characteristics of the second stage of methane transformation on the Fe_4O_6 cluster; however, in this case, the reaction is a one-stage. It is noted that when carrying out various SCF extraction processes, for example, during the purification and regeneration of nickel and iron oxide catalysts, it should be borne in mind that the use of a propane-butane mixture as a supercritical fluid can be accompanied by its saturation with heavier hydrocarbons of linear and branched structure and alcohols. However, in real technological SCF processes, it is realistic to select the optimal temperature and flow regime that minimizes this effect.

In the presence of a pre-reaction complex involving the hydrogen bond of the hydroxyl group of the initial propylene glycol and the interstitial oxygen atom (Fe–O–Fe) of the Fe_4O_7 cluster, a one-stage reaction with the oxidation product 1-hydroxypropan-2-ol becomes possible. The Fe_4O_6 iron oxide cluster with four coordinated iron centers having a hydroxyl group bound to each of them interacts with propylene glycol to form 1-hydroxypropan-2-ol, and the Fe–OH and Fe–O–Fe cluster substructures are the oxidative centers. In this case, the product of the reaction is a water molecule chemisorbed on the iron center and a hydrogen atom chemisorbed on the Fe–O–Fe substructure. This reaction is extremely exothermic (Q = 62.55 kcal·mol^{-1}) and has a very low activation energy for the forward direction of the reaction. By the example of the described heterogeneous hydrate-dissociative effects involving metal oxide surfaces and simple or functionalized

alkanes, it can be seen that it is the protonated and hydroxylated forms of metal oxide surfaces that are responsible for elementary acts related to supercritical water oxidation.

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