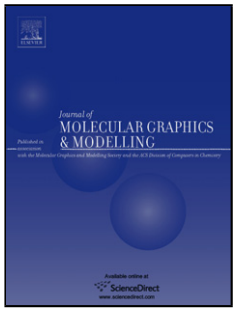


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# Theoretical Investigation of the Selective Dehydration and Dehydrogenation of Ethanol by Molecular Clusters

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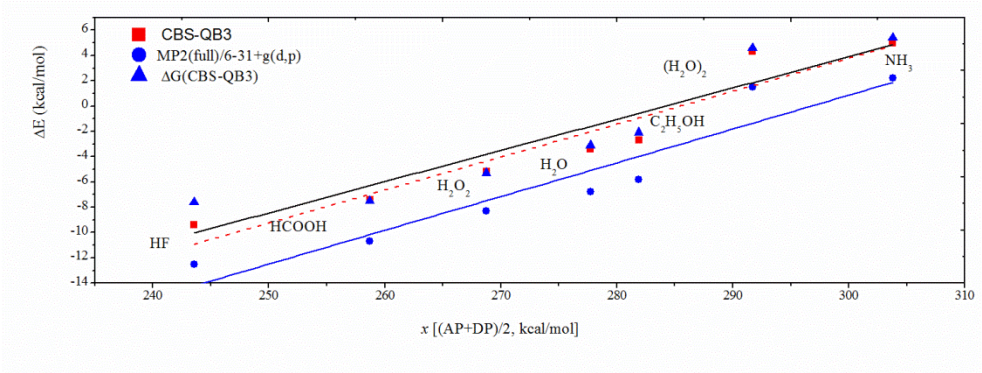
**Graphical abstract**




## Highlights

- Selectivity of catalysts depends on catalysts' acidity and basicity.
- Acidic catalyst prefers dehydration while basic catalysts tend to promote dehydrogenation.
- (3)Solvent- and catalyst-free self-oxidation was an important for selective dehydrogenation

**Abstract:** Catalytic dehydration and dehydrogenation reactions of ethanol have been investigated systematically using the *ab initio* quantum chemistry methods. The catalysts include water, hydrogen peroxide, formic acid, phosphoric acid, hydrogen fluoride, ammonia, and ethanol itself. Moreover, a few clusters of water and ethanol were considered to simulate the catalytic mechanisms in supercritical water and supercritical ethanol. The barriers for both dehydration and dehydrogenation can be reduced significantly in the presence of the catalysts. It is revealed that the selectivity of the catalytic dehydration and dehydrogenation depends on the acidity and basicity of the catalysts and the sizes of the clusters. The acidic catalyst prefers dehydration while the basic catalysts tend to promote dehydrogenation more effectively. The calculated water-dimer catalysis mechanism supports the experimental results of the selective oxidation of ethanol in the supercritical water. It is suggested that the solvent- and catalyst-free self-oxidation of the supercritical ethanol could be an important mechanism for the selective dehydrogenation of ethanol on the theoretical point of view.