

Nano scale surface and reaction mechanism study of (*R*)- and (*S*)-2-butanol over 100 surface alumina: Experimental vs. DFT

Hossein A. Dabbagh, Mehdi Zamani
dabbagh@cc.iut.ac.ir

*Catalysis Research Laboratory, Department of Chemistry, Isfahan University of Technology
 Isfahan, 841548311 Iran*

Reactions of 2-butanol over alumina were investigated under various conditions. The mechanism of dehydration, dehydrogenation, ether formation, hydrogen-shift, and the conformational analysis of adsorbed (*R*)- and (*S*)-2-butanol over the (100) surface of alumina was computed by Density Functional Theory (DFT). Adsorption, dissociation energy, and Mulliken charges were calculated for (*R*)- and (*S*)-2-butanol adsorbed on the surface (100) alumina. Mulliken atomic charges predict that selected basic sites play a major role in elimination reactions. Computed conformational analysis indicates that the (*S*)-isomer forms a stronger bond with the surface than the (*R*)-isomer. Migration of proton of (*S*)-isomer (sc-ap conformer) to oxygen O_c is an endothermic process ($+9.187 \text{ kcal mol}^{-1}$) with small activation energy ($13.560 \text{ kcal mol}^{-1}$). Transition state model, made of two layers of alumina is involved in anti elimination of the sc-sc conformer of (*S*)-2-butanol. E2 elimination with synclinal transition state is comparable with E2 antiperiplanar transition state (Figure 1).

The distance between basic sites of alumina and β , activation energy (E_a), and enthalpy (ΔH°) of the most stable conformers of adsorbed (*R*)- and (*S*)-2-butanol over the (100) surface were calculated to help shed light on the elimination reaction pathway. All basic oxygen sites of the surface at distances less than 4 Å from β hydrogens were considered as a site for elimination and were included in our study.

References:

- [1] H. A. Dabbagh, J. Mohammad Salehi, J. Org. Chem. **63** (1998) 7619.
- [2] H. Pines, W. O. Haag, J. Am. Chem. Soc. **83** (1961) 2847.
- [3] H. Pines, C. N. Pillai, J. Am. Chem. Soc. **83** (1961) 3270.

Figure 1.

