Theoretical study of bonding and vibrational models of the ethoxy radical adsorbed on transition metal surfaces

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Abstract – The ethoxy radical is an intermediate in the selective dehydrogenation of ethanol to acetaldehyde. In spite of the importance of this process little is known about the bonding mode and characteristic vibrational frequencies of this surface species. In the present work we report the results of periodic density functional theory based calculations within the repeated slab model for the adsorption of the radical ethoxy on the (111) surface of various transition metals (Au, Ag, Cu and Pd). Energies, geometries and vibrational frequencies are reported and discussed. It is found that the trend for binding energy is Cu > Ag > Pd > Au. This trend is further analyzed in the framework of the d-band model.

The selective oxidation of alcohols to carbonylic compounds is one of the most important transformations in organic chemistry. It is a surface catalyzed reaction and proceed via the formation of alkoxy free radical intermediates[(1)]. Usually the kinetics of such reactions are followed by Electron Paramagnetic Resonance spectroscopy but, being β-hydride elimination the dominant path for alkoxy or alkyl groups[(1)], for which the unpaired electron is not involved in the reaction, EPR spectra are less useful and a vibrational study of the intermediate radicals is an excellent alternative[(2)]. On the other hand, besides the energetics, to achieve a detailed understanding of any surface catalyzed process the description of the geometry of the reactive species is also necessary[(3)].

In this work binding energies, structure and vibrational frequencies are studied for ethoxy radical adsorbed on the followings transition metal surfaces: Au(111), Ag(111), Cu(111) and Pd(111) using periodic Density Functional Theory (DFT) with the Generalized Gradient Approximation (GGA), ultrasoft psedopotentials and the Projector Augmented Wave formalism to take into account the effect of the cores on the valence electron density included in the Vienna Ab initio Simulation Package (VASP). The metallic surfaces were modeled trough four-layer slabs with vacuum regions of at least 1.2 nm. The potential energy surface of the adsorption models was explored trough the ethoxy radical adsorbed on top, bridge, hcp and fcc hollow surface sites.

It was found the trend for binding energies to be Cu > Ag > Pd > Au and for the distance ethoxy-metal d(O-M) to be Ag > Au > Pd > Cu, the latter correlating linearly with metal atomic size d(M-M) as can be seen in Table 1. These data are analyzed in the framework of the d-band model. Regarding the gas phase, adsorbed ethoxy geometrical parameters change as follows: distance (C-O) increases, distance (C-C) decreases, and angle (C-C-O) closes. Tiltings (C-O) and (C-C) are further analyzed. Finally the calculated vibrational spectra is compared with available experimental data and used to interpret bonding and geometrical changes.

Table 1: Binding energies and geometrical parameters of ethoxy adsorbed on fcc hollow site of transition metal surfaces.

Surface	Distance (M-M) nm	Distance (O-M)nm	B. Energy, eV
Ag(111)	0.293 – 0.304	0.233	2.24
Au(111)	0.285 – 0.295	0.230	1.56
Pd(111)	0.270 – 0.280	0.218	1.91
Cu(111)	0.249 – 0.258	0.207	2.58

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