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Quantum chemical simulation of the gas-phase adsorption of formaldehyde and ionic forms of methylene glycol on the (111) face of Cu, Ag, Au, Pd and Pt

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Abstract

Regularities of the gas-phase adsorption of formaldehyde on Cu, Ag, Au, Pd and Pt surfaces attract attention due to the rapid development of heterogeneous catalysis on transition metals. In this work quantum chemical simulation of the gas-phase adsorption of formaldehyde and ionic forms of methylene glycol on the (111) face of Cu, Ag, Au, Pd and Pt is carried out in the framework of density functional theory (B3LYP hybrid functional). 6-31G(d,p) basis set for H, C and O atoms and LanL2MB pseudopotential for metal atoms were used. Adsorption surface was modeled with the $Me_{31}(19,12)$ cluster. Results indicate weak interaction of formaldehyde with all considered metals. The internal geometric parameters of the adsorbed formaldehyde molecule are identical to those computed for the gas-phase molecule. The obtained results permit to conclude that formaldehyde adsorbs physically on (111) surface of all considered metals. Cationic form of methylene glycol chemisorbs on Cu, Ag, Au, Pd and Pt surfaces with high energetic effect. Adsorption energy of CH_3O^+ decreases in the series: Pd > Pt > Cu > Ag > Au. Cationic form of methylene glycol is bonded to metal through carbon atom which is situated on the top position relative to surface. During optimization of methylene glycol anionic form position on metal surface two possible adsorption states were found. The less stable adsorption state was established only for Cu, Ag and Au surface. For favorable adsorption state adsorption energy decreases in the series: Pt > Pd > Au > Cu > Ag and thus it doesn't correlate with the row obtained for CH_3O^+. The adsorption bond $CH_3O_2^-$/Me is stronger than that of CH_3O^+/Me for all considered metals. In favorable adsorption state anionic form of methylene glycol is bonded to metal through oxygen atom which is situated near the top position relative to surface. It is known that $CH_3O_2^-$ adsorbed on IB-metals and platinum group metals in water solutions dissociates with the formation of atomic hydrogen. In this work the possibility of dissociative gas-phase adsorption of anionic form of methylene glycol was examined. It was shown that $CH_3O_2^-$ dissociates on (111) face of Cu, Pd and Pt with the formation of formic acid anion and two atoms of hydrogen.