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Full Papers

甲醇和甲氧基在**Cu(111)**表面吸附的第一性原理研究

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摘要 采用密度泛函理论(DFT)和广义梯度积分(GGA)的方法，对甲醇和甲氧基(CH_3O)在四种位置(top, bridge, hcp, fcc)的吸附行为进行研究. 分别优化计算了CH_3OH和CH_3O的平衡吸附构型，吸附能，电子结构，Mulliken电荷布居，以及振动频率，结果与实验报道值相吻合. CH_3OH在Cu(111)表面最有利的吸附位是顶位(top)，且C-O键轴倾斜于表面，而垂直吸附于fcc位，保持C_{3v}对称性是最稳定的吸附状态. 对CH_3OH的可能解离路径进行观察计算，并寻找过渡态. CH_3O是甲醇解离的中间体，并且在铜表面发生较强的化学吸附.

关键词 密度泛函理论(DFT), 甲醇,甲氧基,Cu(111)表面,过渡态
分类号

Adsorption of Methanol and Methoxy on Cu(111) Surface: A First-principles Periodic Density Functional Theory Study

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Abstract Adsorption of methanol and methoxy at four selected sites (top, bridge, hcp, fcc) on Cu(111) surface has been investigated by density functional theory method at the generalized gradient approximation (GGA) level. The calculation on adsorption energies, geometry and electronic structures, Mulliken charges, and vibrational frequencies of CH_3OH and CH_3O on clean Cu(111) surface was performed with full-geometry optimization, and compared with the experimental data. The obtained results are in agreement with available experimental data. The most favorite adsorption site for methanol on Cu(111) surface is the top site, where C—O axis is tilted to the surface. Moreover, the preferred adsorption site for methoxy on Cu(111) surface is the fcc site, and it adsorbs in an upright geometry with pseudo-C_{3v} local symmetry. Possible decomposition pathways also have been investigated by transition-state searching methods. Methoxy radical, CH_3O, was found to be the decomposition intermediate. Methanol can be adsorbed on the surface with its oxygen atom directly on a Cu atom, and weakly chemisorbed on Cu(111) surface. In contrast to methanol, methoxy is strongly chemisorbed to the surface

Key words density functional theory methanol methoxy Cu(111) surface transition state

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