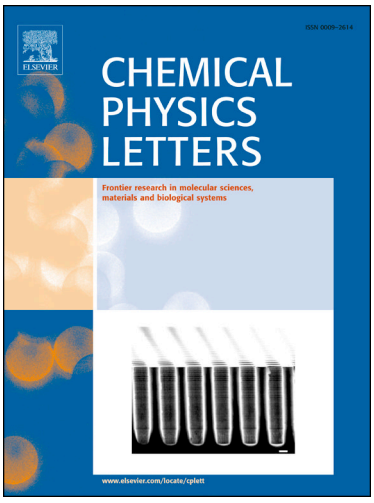

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Interaction Of Aromatic Molecules With Small Gold Clusters

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Abstract

Ab initio density functional simulations have been performed to study the adsorption of aromatic molecules (benzene and toluene) on small Au_n clusters. The calculations reveal a strong interaction between gold and π electrons of benzene, accompanied by a small electronic charge transfer from benzene to gold. We report a variety of binding conformations, with varying degrees of contact between the carbon atoms in benzene and the cluster. Therefore, the interaction between the aromatic part of molecules involved in the synthesis of fine chemicals catalyzed by gold must not be neglected, and could play an important role during some reaction stages.

Keywords: Density Functional Theory, Clusters, Catalysis, Benzene, Adsorption

1. Introduction

Since the discovery by Haruta of a susprising catalytic activity of nano-sized gold particles [1], the possibility of using gold as a catalyst for a broad variety of reactions has attracted an ever increasing interest [2, 3, 4]. Both small Au_n clusters and nanometer-sized gold particles have been found to be active for many reactions, including low-temperature CO oxidation [5, 6, 7], propylene epoxidation [8, 9], NO and SO_2 reduction[10, 11], etc... Also, single Au atoms are routinely used as homogeneous catalysts [12, 13]. One of the most interesting applications of this type of catalysts is the synthesis of fine chemicals[14], a fact of enormous interest for the chemical industry. In many cases, finding simpler alternate routes for the synthesis of some relevant chemicals could help to reduce both the prizes of the products and the ecological impact during their production. Among the many different fine chemicals which can be synthetized using gold catalysts, or that are either reactants or reaction intermediates during the synthesis of other chemicals, there exists a fairly large number of aromatic compounds containing benzenic rings. One important case is the selective oxidation of benzyl alcohol on Au-Pd bimetallic particles reported by Hutchings' group [15, 16], which has motivated numerous recent studies on the ability of gold nanoparticles to selectively produce the desired products [17].

The interaction between benzene and various transition metals (TM) has been intensively studied in the past [18, 19], with TM-benzene sandwich compounds known to have many potential applications in nanotechnology [20]. In the case of gold, while the benzene interaction with extended gold surfaces has been widely studied [21, 22, 23, 24, 25], there is much less information in the case of small clusters and nanoparticles, specially from a theoretical point of view. Recent simulations of the adsorption of benzene on the Au(111) surface [26] and of the interaction of benzene with the Au^+ cation [27], as well as experiments, show that benzene is easily adsorbed on small Au cluster cations [28]. Since adsorption of aromatic compounds on gold catalysts constitutes the first stage of many important reactions for the synthesis of fine chemicals, it would be interesting to get a deeper insight into the interaction of the π system of benzene with small Au clusters. With this purpose, we have performed Density Functional Theory (DFT) simulations of the adsorption of benzene and toluene on Au_n clusters. We have analyzed the influence that the charge state of the cluster has on the adsorption features, as well as the effect of the presence of a substituent group. The results show that in most cases the π electron cloud of benzene interacts strongly with the gold cluster; therefore, this effect needs to be taken into account when studying the initial adsorption of aromatic compounds in catalytic reactions involving these compounds.

2. Computational setup

The *ab initio* DFT simulations of benzene and toluene adsorption on gold clusters were carried out using the DACAPO code [29], in which the electronic wavefunctions are expanded in a basis set of plane-waves [30], and ultrasoft pseudopotentials [31] are used for treating the electron-ion interaction. The PBE functional [32] was used for exchange-correlation, and a cutoff energy of 25 Ryd was employed for the plane waves expansion of the wave functions. It was verified that such cutoff value gives binding energies which are converged within 0.02 eV. Since for these systems dispersion interactions are expected to be non negligible, we have added Grimme's DFT-D3 dispersion correction[33] to the DFT-PBE binding energies (reporting also the pure PBE binding energies in order to show the magnitude of the dispersion corrections).

Large unit cell lengths were used in every direction, in order to prevent sizable mutual interactions between the cluster-adsorbate complexes in neighbouring unit cells. In the case of

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