Vibration of small molecules on Pt(1 1 1) surface

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Abstract

The adsorption of methanol and other small molecules onto transition metal surfaces is an important issue in electrochemistry, fuel cells, etc. Despite the overwhelming interest there are still unresolved issues beginning from the geometry of the adsorbed species to the correct assignments of different vibrational modes of the adsorbed molecules on the surface.

In order to understand the adsorption processes, we have performed density functional theory (DFT) calculations for small molecules (methanol, formaldehyde, formic acid) on Pt(1 1 1) surfaces. We investigated the nature of the metal–ligand bonding in these adsorption processes using electron density difference and PDOS (partial density of states) methods. Ab initio vibration spectra have been calculated for these systems.
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1. Introduction

The oxidation of small organic molecules has been widely studied owing to fundamental interest and relevance to fuel cell technology [1,2]. Among these molecules, HCOOH, HCHO and CH_3OH have attracted the most attention of the scientific community because of their simple structure and the relative simplicity of investigation and interpretation of the results. There are several results which show that methanol on group VIII transition metal surfaces (Pt(1 1 1) [3,4], Pd(1 1 1) [5,6], Pd(1 0 0) [7], Rh(1 1 1) [8,9] and Ru(0 0 0 1) [10,11]) decomposes directly to adsorbed CO and H atoms.

The methoxy intermediate was only on Pt(1 1 1) [4] and Rh(1 1 1) [9]. It was found that on Pd(1 1 1) formaldehyde species formed on the surface during the decomposition. Adsorbed methanol transformed into formate in the presence of molecularly adsorbed oxygen [4].

Formaldehyde can coordinate to the metal surface through the oxygen lone pair in η^1 and in $\eta^2(C,O)$ dihapto-configuration. Formaldehyde easily decomposes and polymerizes on clean Pt(1 1 1) [12], Rh(1 1 1) [13], and Pd(1 1 1) [14] surfaces. η^1 formaldehyde was found, during the decomposition of methanol, on Pt(1 1 1) in the presence of oxygen. On Ru(0 0 0 1) surface, Barros et al. [10] also found $\eta^2(C,O)$ formaldehyde during the methanol decomposition. Assignation of these species was performed by different infrared spectroscopy methods (IRAS, RAIRS, HREELS).

Formic acid decomposed at low coverage via dehydrogenation, and it formed catamers upon adsorption at high coverage. The formation of the hydrogen bonded catamers is suppressed in the presence of atomic oxygen. This behavior was found on Pd [15], Pt [16], and Rh(1 1 1) [13,17] surfaces.

Our main goal in this paper is to try to understand the interaction between methanol, formaldehyde, formic acid and Pt(1 1 1) surface using theoretical methods. The adsorption of these molecules on the surface is the first step in their decomposition pathway. We also want to assign all of the vibrational frequencies of the adsorbed species.

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2. Computational details

All adsorption energies as well as the electronic and vibrational properties were calculated by using the Vienna Ab Initio Simulation Package (VASP) [18,19], which is a density functional theory (DFT) code with plane wave basis set. Electron–ion interactions were described using the projector-augmented wave (PAW) [20] method, which was expanded within a plane wave basis set up to a cutoff energy of 400 eV. Electron exchange and correlation effects were described by the Perdew–Burke–Ernzerhof (PBE) [21] GGA type exchange-correlation functional. The total energy of platinum had a minimum at 3.989 Å lattice constant, which is close to the experimental value (3.912) [22]. This lattice constant was used for all calculations.

Geometry optimizations were performed on a supercell structure using periodic boundary conditions. The 1 1 1 surfaces were generally modeled using a $3 \times 2\sqrt{3}$ supercell. The metal slab was chosen to be three atomic layers thick, and a 15 Å vacuum layer was used to ensure that there were no interactions between the surface adsorbates on one layer and the next slab. We examined the adsorption of methanol over three, four and five layer Pt(1 1 1) slabs. The difference of binding energies for methanol over these slabs were calculated to be less than 0.02 eV. For the calculation of work functions and vibrational intensities, a dipole correction scheme was used. The first metal layer was allowed to relax, while the bottom two layers of Pt atoms were held fixed in their bulk position. All atomic coordinates of the adsorbed species and the metal atoms in the relaxed metal layers were optimized to a force of less than 0.025 eV/Å on each atom. Brillouin zone integration was performed using a $3 \times 3 \times 1$ Monkhorst–Pack [23] grid and a Methfessel–Paxton [24] smearing of 0.2 eV.

Vibrational properties of adsorbed species were calculated by applying the finite-difference method to create the Hessian matrix, which was diagonalized to obtain the characteristic frequencies of the system. For this purpose, we used an atomic displacement of 0.01 Å in the three directions of space for the adsorbate and the first metal layer. We calculated the dipole activity, which is related to the intensity obtained in RAIRS and HREELS spectra. This is proportional to the square of the dipole moment variation with respect to the surface normal for the corresponding mode.

3. DFT calculations

3.1. Methanol

It has already been shown that the methanol molecule binds through its oxygen atom in an on-top position to the transition metal surfaces [25–27]. At 1/12 ML coverage the calculated binding energy is 0.32 eV, which agrees well with the results of Greely and Mavrikakis [26,27] (0.33 eV), but differs significantly from the results of Desai et al. [25] (0.45 eV). Fig. 1a illustrates the general binding mode of methanol. The structural parameters and the adsorption energies are given in Table 1. In this most favorable configuration, two methyl hydrogens are pointing towards the Pt(1 1 1) surface similarly to the results of Greeley et al. [25]. In the metastable configuration, when only one methyl hydrogen is pointing to the surface the binding energy is about 0.05 eV smaller than in the global minimum. It is
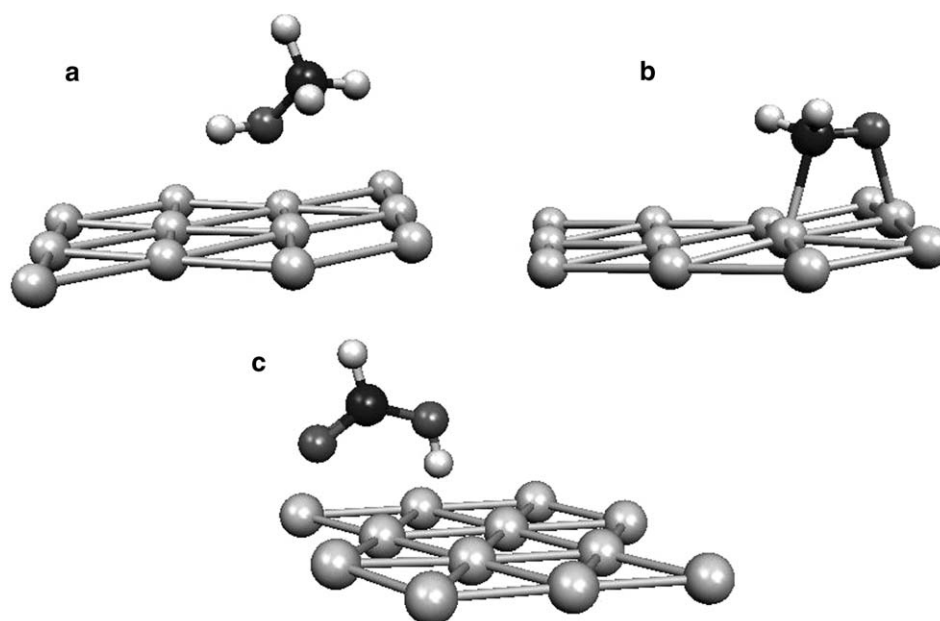

Fig. 1. Calculated equilibrium structure of methanol (a), formaldehyde (b) and trans formic acid (c) adsorbed on Pt(1 1 1). (Oxygen: dark grey, carbon: black, hydrogen: lightest.)