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First principles study of the conformations of cinchonidine on a Pt(111) surface

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Abstract

The conformations of cinchonidine (CD) adsorbed on a Pt(111) surface were studied using first-principles methods. Eight conformationally different adsorption states due to different degrees of rotation around the τ_1 and τ_2 degrees of freedom were identified and their possible role in the formation of chiral surface sites relevant to enantioselective hydrogenation investigated in light of the currently existing experimental evidence. Comparison of the conformational behavior of CD in solution and on platinum has revealed the effect of the metal surface on the internal mobility of the alkaloid. Although the study corroborates the outstanding role of the adsorbed Open(3) conformer suggested previously, the rich conformational flexibility observed on the platinum surface points to the possibility that other conformers of CD also may be involved in enantiodifferentiation. Closed conformations of CD are found to play an important role in the conformational equilibria on the surface due to their stability and are identified as precursors of the less stable, but presumably more active, open conformers. Although the open and closed conformers are closely related to the correspondent ones found in solution, surface species that are also adsorbed via quinuclidine moiety are characteristic of the metal–modifier interaction and should serve as precursors to catalytically active conformations.

Keywords: Cinchonidine; Conformational analysis; Adsorption modes; Platinum; Enantioselective hydrogenation; DFT

1. Introduction

The asymmetric hydrogenation of ketones on cinchona alkaloid platinum catalyst is a promising route for the synthesis of enantiopure and enantioenriched alcohols [1–3]. The advantages, both technical and economic, of heterogeneous catalysis are well known and justify the intense interest in this versatile reaction system [4]. Although several proposals have been advanced concerning the reaction mechanism that leads to the observed selectivity of cinchona-modified platinum, this remains a matter of active debate [1,2]. At least one fact is almost universally accepted: that cinchonidine (CD) or another cinchona alkaloid or synthetic analog [5–8] generates chiral sites on the metal surface that are able to discriminate between the *re* and the *si* faces of a prochiral ketone. To open the door to predictive computations, any mechanistic model should be able to describe such sites to identify which prochiral face of a ketone best fits the interaction with the modifier. Given the conformational complexity of CD, we expect that several chiral sites can be generated on its adsorption on the metal. Using a first-principles approach is a particularly demanding task in this case because, even neglecting the effect of the solvent, it involves the computation of a three-component system characterized by the surface, the modifier, and the substrate. In particular, calculating the metal surface makes a first-principles approach a domain of nonstandard computations, because the large number of electrons of the metal can be treated only using highly parallel computer resources, and the necessary inclusion of relativistic effects becomes compelling [9]. A recent review analyzing the use of computer simulations in enantioselective heterogeneous catalysis concluded that predicting selectivities in such three-component systems demands computer resources beyond the scope of most computational chemists [11]. We have nevertheless attempted to address the problem using a stepwise approach, studying the chiral sites generated by the alkaloid on a platinum surface, temporarily reducing the problem to

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a two-component system. CD has a complex conformational behavior in solution that has been extensively studied both experimentally and computationally [12–15]. In most models the behavior in solution of the alkaloid has been extended to the metal surface, thereby neglecting conformational biases due to the interaction with the metal. Adsorption of the alkaloid on platinum has been studied both experimentally [16–20] and computationally [21–23], but a complete description of the adsorption modes and relative energies of the CD conformations on platinum is not yet available. In the present investigation, we analyzed the possibly complete set of conformations that CD can assume on Pt(111) using a large metal cluster approach for simulation of the surface. We report remarkable differences with respect to the conformational behavior in vacuum or in solution that can provide the basis for the observed selectivity of the catalyst.

2. Methods

2.1. Computational methods

The adsorption studies were performed using the platinum cluster shown in Fig. 1 formed by 38 platinum atoms. All of the cluster calculations were done using the Amsterdam Density Functional program package [24]. A frozen core approximation was used for the inner core of all atoms. The orbitals up to 1s were kept frozen for all second row elements, whereas the orbitals up to 4f were kept frozen for platinum. Decreasing the Pt frozen core to 4d (which implies the explicit calculation of 14 additional electrons per platinum atom) has been shown to increase the adsorption energy by only about 5 kJ/mol for the adsorption of benzene [25]. The importance of relativistic effects has been shown for calculations involving platinum [9,10]. The core was modeled using a relativistically corrected core potential created with the DIRAC utility in the ADF program. The DIRAC calculations imply the local density functional in its simple X-α approximation without any gradient corrections, but the fully relativistic Hamiltonian is used, including spin–orbit coupling. Relativistic scalar approximation (mass-velocity and Darwin corrections) was used for the Hamiltonian with the zero-order regular approximation (ZORA) method [26], which includes spin–orbit coupling in zero order. The first-order Pauli formalism [27] was shown to have theoretical deficiencies due to the behavior of the Pauli Hamiltonian at the nucleus, which led to variational collapse [28] for increasing basis set size. It was shown that the scalar relativistic correction could account for up to 70% of the total energy in the adsorption of carbon monoxide on platinum, and that also the calculated adsorption site was influenced by the use of a relativistic correction [9]. The ZORA formalism requires a special basis set that includes much steeper core-like functions implemented in the code. Within this basis set, the double-ζ (DZ) basis functions were used for platinum, and double-ζ plus polarization (DZP) basis functions were used for second-row elements. The local part of the exchange and correlation functional was modeled using a Vosko–Wilk–Nusair [29] parameterization of the electron gas. The nonlocal part of the functional was modeled using the Becke correction [30] for the exchange and the Perdew correction [31] for the correlation. Energies of surface conformers are reported as energy differences between the total electronic energy of the calculated structures (cluster plus adsorbed alkaloid) and the energy of a reference conformation [SC(1)], which was set to zero. Adsorption energies were calculated with respect to the Open(3) conformer of CD, using the following equation:

$$\Delta E_{\text{Ads.}} = E_{\text{Cluster+Adsorbate}} - E_{\text{Cluster}} - E_{\text{Free Molecule}},$$

where $E_{\text{Cluster+Adsorbate}}$ is the energy of the cluster with the molecule adsorbed, E_{Cluster} is the energy of the isolated cluster, and $E_{\text{Free Molecule}}$ is the energy of the free molecule. All calculations were run unrestricted. The bond distance for the platinum was fixed to the experimental value of 2.775 Å for bulk metal [32]. Molden [33] was used as graphical interface.

3. Results

The following description of the conformations of CD on platinum is based on the usual parameters (angles τ_1 and τ_2) used for defining the conformations of CD in vacuum and in solution [12–15]. As shown in Fig. 2, the angle τ_1 describes the rotation of the quinoline around the C(4′)–C(9) bond, whereas τ_2 describes the rotation of the quinuclidine moiety around the C(9)–C(8) bond. Here we define τ_1 and τ_2 by the dihedral angles C(8)–C(9)–C(4′)–C(4a′) and N–C(8)–C(9)–C(4′), respectively. The directions of rotation are also shown in Fig. 2, which defines the positive values for the angles. Throughout the paper, the rotations around the angles τ_1 and τ_2 are assumed to

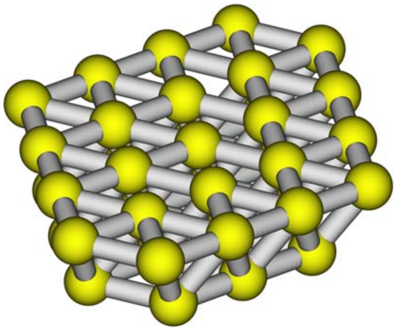

Fig. 1. The platinum 38 cluster used for simulation of a platinum surface.

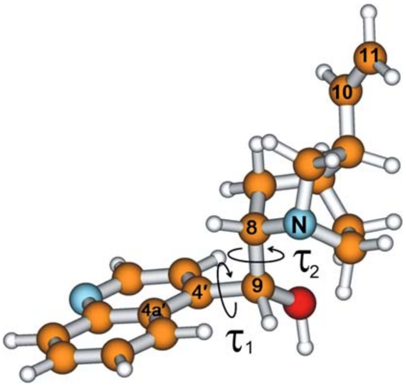

Fig. 2. Definition of the angles τ_1 and τ_2 used for the description of the conformational flexibility of cinchonidine.