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ScienceDirect
Applied Surface Science 252 (2006) 7515–7522
applied surface science
www.elsevier.com/locate/apsusc

A bonding study of c-C_5H_8 adsorption on Pt(1 1 1)

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Received 23 May 2005; received in revised form 2 September 2005; accepted 4 September 2005
Available online 10 October 2005

Abstract

The chemisorption of cyclopentane (c-C_5H_8) on Pt(1 1 1) has been studied using a qualitative band-structure calculations in the framework of tight-binding implementation with the YAeHMOP package. We modeled the metal surface by a two-dimensional slab of finite thickness with an overlayer of c-C_5H_8, in a (3 × 3) di-σ geometry. The c-C_5H_8 molecule is attached to the surface with its C=C atoms bonded mainly with two Pt atoms while the opposite CH_2 bends towards the surface. The Pt–Pt bonds in the underlying surface and the C–C bonds of c-C_5H_8 are weakened upon the chemisorption. A noticeable Pt–H and Pt–C interactions has been observed. We found that of Pt $5d_z^2$ band plays an important role in the bonding between c-C_5H_8 and the surface, as do the Pt 6s and $6p_z$ bands. The HOMO-LUMO bands of c-C_5H_8 are very dispersed, indicative of a strong interaction with the metal surface.

Keywords: Platinum; Cyclopentane; Adsorption; Molecular orbital

1. Introduction

The study of molecules adsorbed on platinum surfaces is important from both a practical and theoretical point of view. Platinum is one of the most versatile heterogeneous metal catalysts. Its chemical stability in both oxidizing and reducing conditions makes it a very convenient election in a lot of petrochemical applications. The use of Pt–Al_2O_3 catalyst for naphtha reforming is well known from the 1950s [1]. The reactions of cyclic hydrocarbons on Pt(1 1 1) surfaces have been extensively investigated owing to their importance in petroleum reforming processes. The dehydrogenation of cyclic alkanes and alkenes to aromatic hydrocarbons is particularly significant in the efficient production of fuels, since such processes increase the octane number of fuel mixtures. A complex network of isomerization, hydrogenation, dehydrogenation and hydrocyclization steps takes place during reforming. Several of these reactions have C_5 intermediates. A number of studies of this class of molecules on Pt have been performed as a first approach to describe the structure and the chemical behavior of such intermediates [2–13]. In preliminary theoretical studies, Brizuela et al. have investigated the adsorption of C_5H_n (n = 10, 8 and 5) rings on Pt(1 1 1) [14–17]. In the case of c-C_5H_8 that

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doi:10.1016/j.apsusc.2005.09.002

the geometry suggested by Avery [5–7] that includes a tilted adsorption and sp^3 rehybridization of the double bond carbons was considered. Recently, Becker et al. [18] published a very interesting experimental and theoretical determination of the adsorption site of c-C_5H_8 on Pt and PtSn surface alloys. They considered a di-σ geometry where the double bond interacts with two Platinum atoms (the median carbon lies above a third Pt atom) and π geometry where the double bond interacts with only one metal surface atom. These authors find that the π adsorption is less stable than the di-σ one by 26–30 kJ/mol for all coverage, which confirms the experimental finding.

The objective of the present work is to study the chemisorption of c-C_5H_8 on Pt(1 1 1) at low coverage, including the changes in the molecular orbitals and bonding of the absorbate and the metal orbitals which participate in the bonding. The model is discussed in the next section.

2. The adsorption model

Our electronic structure calculations were performed using the extended Hückel method, an approximate molecular orbital scheme, implemented with the YAeHMOP package [19]. This method captures the essential orbital interactions in chemisorption well. The density of states (DOS) of both c-C_5H_8 and Pt and the crystal orbital overlap population (COOP) curves between atoms and orbitals were calculated in order to analyze the adsorbate–surface interactions. The COOP curve is an energy-resolved plot of the overlap population-weighted density of states. Integration of the COOP curve up to the Fermi level gives the total overlap population (OP). When computing the DOS and COOP, we modeled the system by a two-dimensional slab of finite thickness so as to better simulate the semi-infinite nature of the metallic surface. A periodic four-layer slab was employed as a compromise between computational economy and reasonable accuracy. One molecule is adsorbed per unit cell on one side of the slab. We used the same geometric periodicity of bulk Pt and no reconstruction was included for the first layer. A unit cell of nine Pt atoms per layer was considered giving a (3 × 3) structure and a cyclopentane coverage of 1/9 ML. Our calculation indicates that for this coverage there is no adsorbate–adsorbate interaction. The 1/7 ML ($\sqrt{7} \times \sqrt{7}$ $R19^\circ$) gives a similar electronic structure and bonding results. The 1/4 ML (2 × 2) was not considered because its computed adsorption energy is much lower than the experimental finding [18]. The adsorption geometry was the one determined from ab initio calculations by Becker [18]. As mentioned in the Introduction, a di-σ geometry is preferred. Fig. 1a shows the c-C_5H_8 in this configuration on a three-fold tetrahedral hole (3CT). The middle methylene group (C_4) is bended to the metal surface lying on the Pt_1 atom (see Fig. 1b). The molecule, which is planar in the gas phase results distorted upon adsorption and undergoes a substantial $sp^2 \rightarrow sp^3$ rehybridization of olefinic carbon orbitals in a configuration designated as η^2-di-σ-c-C_5H_8 [5,6,18].

We used a bending angle ω of the cyclopentane (angle between $C_1C_3C_4$ and $C_2C_4C_5$) of 148° and a α

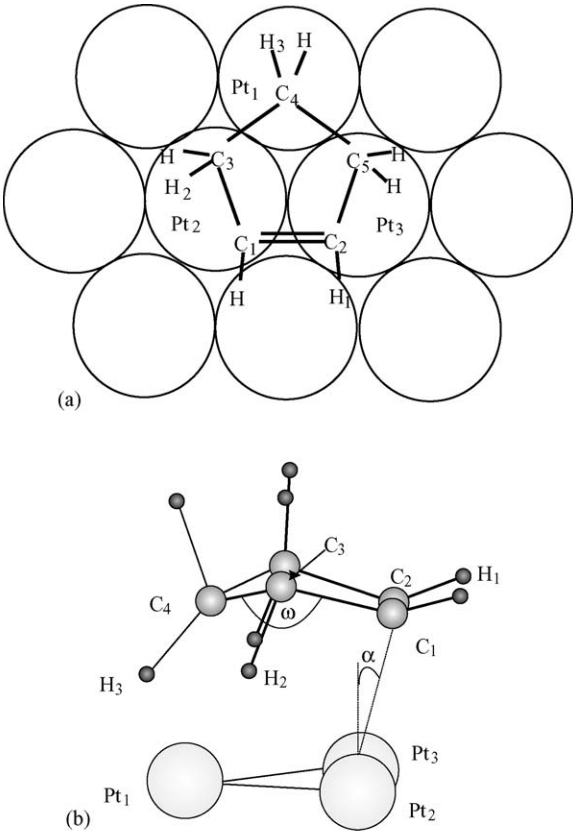

Fig. 1. Numbering of atoms of 3CT-C_5H_8/Pt(1 1 1) (a); side view of the local adsorption geometry (b).