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Growth mechanism of palladium clusters on rutile $TiO_2(110)$ surface

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Abstract

Oxide-supported transition metal systems have been the subject of enormous interest due to the improvement of catalytic properties relative to the separate metal. Thus in this paper, we embark on a systematic study for Pd_n ($n = 1-5$) clusters adsorbed on $TiO_2(110)$ surface based on DFT-GGA calculations utilizing periodic supercell models. A single Pd adatom on the defect-free surface prefers to adsorb at a hollow site bridging a protruded oxygen and a five-fold titanium atom along the $[\bar{1}10]$ direction, while Pd dimer is located on the channels with the Pd–Pd bond parallel to the surface. According to the transition states (TSs) search, the adsorbed Pd trimer tends to triangular growth mode, rather than linear mode, while the Pd_4 and Pd_5 clusters prefer three-dimensional (3D) models. However, the oxygen vacancy has almost no influence on the promotion of Pd_n cluster nucleation. Additionally, of particular significance is that the Pd-TiO_2 interaction is the main driving force at the beginning of Pd nucleation, whereas the Pd–Pd interaction gets down to control the growth process of Pd cluster as the cluster gets larger. It is hoped that our theoretical study would shed light on further designing high-performance TiO_2 supported Pd-based catalysts.

Key words

density functional theory; $TiO_2(110)$ surface; palladium cluster; adsorption

1. Introduction

Oxide-supported transition metal systems have attracted enormous attention in recent decades, which are of great interest in view of their applications in photocatalysis [1−3] and heterogeneous catalysis [4−7]. One of the most appealing challenges for material scientists, nowadays, is investigating the intrinsic nature of such interfaces [8−18].

Owing to the technological applications, titanium dioxide has evolved into one of the best investigated oxide materials and is generally used to model TiO_2 catalytic properties under ultra-vacuum (UHV) conditions in surface science [19−23]. TiO_2, existing in three main crystalline forms (rutile, anatase, and brookite), is known to have the tetragonal $P4_2$/mmm space group [6] in the rutile phase. From a theoretical point of view together with an experimental one, the rutile $TiO_2(110)$ surface is taken to serve as a substrate of great interest due to its highest stability [24,25]. On the other hand, palladium-supported catalysts are used in important processes due to its high affinity toward metal oxide surfaces [26,27]. Such a linkage between titanium dioxide and palladium, if established, is of huge incentive.

Experimentally, considerable efforts have been done in the development of Pd-$TiO_2(110)$ system in the past decade [28−35]. Della Negra and co-workers [29] have investigated the bonding mechanism and the electronic properties of the Pd-$TiO_2(110)$ system via photoelectron spectroscopy (core levels and valence band) and resonant photoemission. Chang et al. [33] studied the effect of adsorbed Pd on HCOOH/$TiO_2(110)$ at room temperature by means of high-resolution electron energy-loss spectroscopy (HREELS). Additionally, Howard et al. [31] have synthesized Pd nanoclusters on $TiO_2(110)$ and observed the evolution of the size distribution by scanning tunneling microscopy (STM).

However, to our knowledge, the number of theoretical work addressing the Pd/$TiO_2(110)$ system is relatively scarce [36−39]. Bredow et al. [36] studied Pd atoms and dimers supported on $TiO_2(110)$ surface, and found that the preferred adsorption sites for Pd atoms were the five-fold titanium rows at the perfect rutile $TiO_2(110)$ from the DFT-B3LYP slab calculations while the two-coordinated protruded oxygen atoms were the most stable adsorption sites from embedded cluster

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models. Moreover, there was no Pd-surface interaction after correcting the basis set superposition error (BSSE) from Hartree-Fock (HF) calculations. However, Sanz and Márquez [39] reported contradictory results according to their investigation on the Pd/TiO_2(110) system using periodic supercell models within DFT-GGA calculations. They found that Pd-isolated atoms and dimers on the defect-free rutile TiO_2(110) surface preferred to adsorb on the surface channels near the five-fold titanium atoms but tilted toward the protruded oxygen atoms while Pd dimers exhibited a noticeable metal-metal interaction. Furthermore, for the defective surface, they reported that the adsorption of Pd atoms at surface oxygen vacancies was stronger than that on the perfect surface.

Considering the controversy about the mechanism, it is intriguing that more theoretical investigations on the Pd/TiO_2(110) system are compulsory. In the present work, to obtain a comprehensive understanding on the nucleation mechanism of Pd_n ($n = 1-5$) clusters adsorbed at the defect-free and defective rutile TiO_2(110) surfaces, we carried out a detailed survey based on DFT-GGA calculations performed under periodic supercell conditions. In addition, the system of CO catalytic oxidation on Pd_n/TiO_2(110) will be discussed in our next work. The results obtained here can hopefully shed light on further designing high-performance TiO_2-based catalysts and thus are of general interest to chemistry.

2. Computational details

All the density functional theory (DFT) [40−43] calculations were performed utilizing the Perdew-Wang (PW91) exchange-correlation functional [44] as implemented in the Dmol^{3}software [45,46], in which the physical wave functions were expanded in terms of accurate numerical basis sets. The generalized gradient approximation (GGA) [47] was chosen here, because it's better than the local density approximation (LDA) for Pd/metal oxide system [39] and the energetics of molecular adsorption [48,49]. Double numerical with polarization (DNP) [50,51] basis sets were employed, expanding the valence electrons functions into a set of numerical atomic orbitals. Furthermore, the use of numerical basis sets minimizes the basis set superposition error (BSSE) [52]. During the computation, the inner electrons of Pd atoms were kept frozen and substituted by an effective core potential (ECP). Brillouin-zone integrations were performed using $2\times3\times1$ Monkhorst-Pack grid [53] and a Fermi smearing of 0.005 Hartree. The tolerances of energy, gradient, and displacement convergence were 2×10^{-5} Hartree, 4×10^{-3} Hartree/Å, and 5×10^{-3} Å, respectively. In addition, transition states (TSs) were searched by utilizing the complete linear synchronous transit and quadratic synchronous transit (LST/QST) method. The calculated pathways can determine various states along a surface reaction pathway (e.g., the initial state (IS), TS and the final state (FS)) and provide important information about the reaction mechanism.

Many other literatures [54−59] showed that nine atomic layers slab was enough to simulate the rutile (110) surface. Thus, in this work, a periodic slab containing nine atomic layers was adopted by (3×1) supercell. The side and top views of this system were shown in Figure 1b and 1c. All the atoms in this whole system (adsorbate/substrate) were allowed to relax in all directions, except for the atoms at the bottom six layers which were hold at their bulk-truncated structure. A vacuum layer thickness of 10 Å [39,60] has been checked enough to prevent any noticeable interaction between two successive slabs. During the calculation, the (3×1) supercell, and the vacuum layer thickness as well as the numbers of layers are judged to be adequate to yield good convergence of energies and properties, indicating that our computational approach was reasonable.

To describe the interaction between the adsorbed Pd clusters and TiO_2(110) surface, we calculated the binding energies according to the expression

$$E_{\text{bind}} = -[E(\text{Pd}_n\text{-TiO}_2) - E(\text{TiO}_2) - E(\text{Pd}_n)] \qquad (1)$$

where, $E(\text{Pd}_n\text{-TiO}_2)$, $E(\text{TiO}_2)$, and $E(\text{Pd}_n)$ are the total energy of the adsorbate/substrate system, the energy of bare TiO_2(110) surface, and the energy of free Pd_n cluster in gas phase, respectively. Additionally, n represents the number of adsorbed Pd atoms.

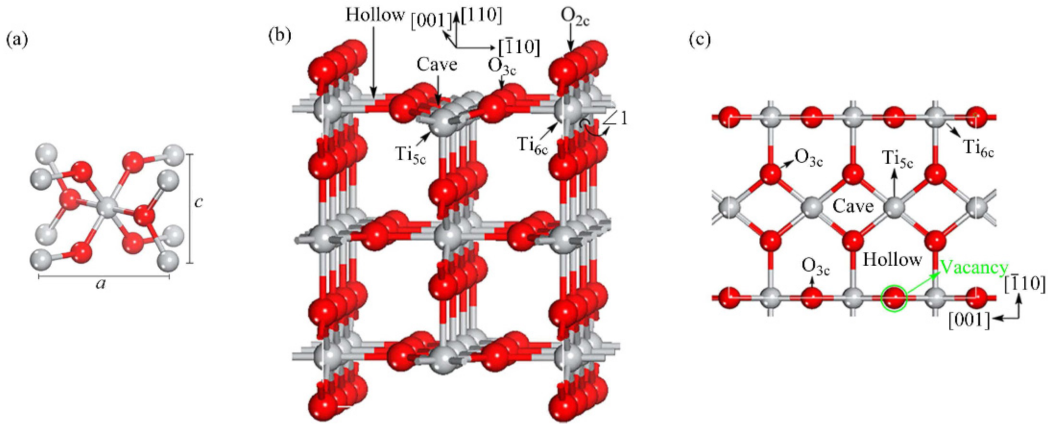

Figure 1. Unit cell of rutile (a) bulk structure and TiO_2(110) surface model, (b) side view and (c) top view. The letters are used for identification purposes