Water adsorption and desorption processes on the α-quartz(0001) surface: a density functional theory and kinetic study

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Abstract

Water covers free solid surfaces and moreover it plays a key role in electrochemistry, catalysis and electronic devices. So, the understanding of the water reaction on oxide surfaces is important. On the other hand, α-quartz is an abundant mineral on earth and it is technologically important, for example, due to its piezoelectricity properties. Therefore, the water-silica system plays a significant role in material chemistry.[1−3] In this work, we present a theoretical study of the adsorption and desorption of water on the α-quartz(0001) surface, in particular, a cleaved surface (or a bare surface) and a hydroxylated surface, where the first and the last layers of the α-quartz are covered by hydroxyl groups that saturate the dangling bonds. We have performed density functional theory (DFT) calculations by means of the VASP code[4,5] with the generalized gradient approximation (GGA), using the PW91 functional. Our results show that water adsorbs by dissociation on the cleaved surface, which is very reactive. The adsorption energy is 3.374 eV. On the hydroxylated surface, water adsorbs molecularly through hydrogen bonds formed between water and the hydroxyl groups with an adsorption energy of 0.740 eV. Clearly, the adsorption process depends on the kind of the α-quartz(0001) surface considered. Moreover, we have computed the minimum energy path for the dissociation reaction on the cleaved surface and the desorption reaction on the hydroxlated surface. The results show that neither of the reaction barriers possesses a maximum. We have calculated the rate constants for the hydroxylated surface. It is observed that water desorption is a slow process in agreement with some available experimental measurements.

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Complex reaction networks in the conversion of ethylene to ethylidyne on flat and stepped Pd

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Abstract

Adsorption and conversion of ethylene to ethylidyne on flat and stepped Pd surfaces have been studied by means of Density Functional Theory with the aim to understand the complex chemistry of small organic molecules on Pd. These processes are crucial to understand the experimental observations of the presence of a C subsurface layer in the active palladium catalysts recently reported by Teschner et al.[1] but they are also involved in selective hydrogenations, steam reforming, polymerization and several other chemical processes on these catalysts.

Our results provide a view on the complex chemistry of olefins on the surface where several competitive processes take place simultaneously and where a hierarchy among different bond activations can be established. The results show how under low coverage ethylene and its derivatives hydrogenation-dehydrogenations are the most likely processes on both surfaces. This differs from Ni for which a more pronounced step effect in terms of the selectivity for the activation of C-H or C-C processes was observed.[2] In addition, isomerization processes are energetically very costly and thus are not likely to take place under relevant operation conditions. Instead moieties containing CH_3 fragments are generated by indirect processes the most likely related to the scrambling of hydrogen atoms on the surface. According to our results, the hydrogen related processes in ethylene decomposition on the Pd surface, excluding the isomerization, seem to follow the Brønsted-Evans-Polanyi[3,4] type of behaviour.

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Charge transfer excitation energies in pyridine-silver complexes studied by QM/MM methods

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Abstract

We utilize DFT based quantum mechanical/molecular mechanical (QM/MM) approaches for the investigation of charge transfer (CT) excitations in molecule-metal systems. We perform model calculations on a $pyridine - Ag_{20}$ system, treating the most distant silver atoms using molecular mechanics by assigning atomic polarizabilities to each of these silver atoms. The QM/MM method for molecule-metal systems involves the implementation of two kinds of damping: (i) between the MM induced dipole moments and (ii) of the QM electric field at the polarizable MM sites. We present a procedure for determining the damping coefficients. We investigate how additional silver layers affect the CT excitation energy. Moreover, we investigate how the change in distance between pyridine and silver clusters shifts the CT excitation energy.

Selectivity in the Ostwald process: A theoretical approach

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Abstract

The Ostwald process is used commonly in chemical industry for HNO3 production. A first principles study on the selectivity of NO towards N2 production on this process has been developed for a set of metals. The thermochemistry and kinetic data for the key reaction steps have been calculated by means of Density Functional Theory and utilized in a kinetic model. Ab-initio thermodynamics has been used to show thermodynamic stability differences between the PtRh alloy and pure metals Pt and Rh. This is an important factor at the reaction conditions: high O2 pressure and high temperature. All these calculations have been applied in order to predict the performance of the industrial catalyst.

TEMPLATE EFFECTS IN VINYL ACETATE SYNTHESIS ON PdAu SURFACE ALLOYS: A DFT STUDY

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Abstract

Vinyl acetate, VA, is a major industrial product involved in the manufacture of polymers. It is synthesized from the coupling of acetic acid and ethylene in oxygen ambient. Recently, isolated Pd dimers on Au surfaces have been found to be active and selective catalysts for the process but a strong dependence on the local structure of the ensemble is observed.[1] By means of Density Functional Theory, we demonstrate how the most successful ensemble shows the best performance on different steps: easy adsorption of reactants, inhibited poisoning and low barrier for the rate limiting step.[2]

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Wetting of Nanostructured Polymer Surfaces

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Abstract

The wettability plays a central role in nature, everyday life, and technical applications. The combination of chemical composition and topographical structure determine the surface wetting properties. Hierarchical micro- and nanostructures are responsible for the extreme water-resistance frequently observed in the plant and animal worlds. The roughness-induced hydrophobicity has attracted considerable attention due to the remarkable self-cleaning and antiadhesive properties. Upgrading of widely used plastics by mimicking nature's structured surfaces could provide novel products with high value added. First, however, comprehensive understanding of phenomena is required to enable optimization of surface structures for specific wettability.

We have used molecular dynamics simulations to study the wetting of nanostructured polyethylene (PE) and polyvinylchloride (PVC) surfaces by water. The influence of controlled one- and two-dimensional roughness with different dimensions on droplet contact angle, equilibrium state and shape, and dynamic behavior was studied.[1−3] The employed models were validated through the simulated water contact angles on smooth polymer surfaces.[4] The observed phenomena at the simulation scale were in good agreement with experiments and the predictions of macroscopic theories. The understanding of congruencies and differences due to different length scales enables the future use of simulations for optimization of surface roughness and prediction of wetting behavior on new materials.

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Towards full atomistic simulation of gold-thiol systems

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Abstract

Self-assembled monolayers of thiols on gold surfaces have a wealth of applications in nanotechnology.[1] The gold-sulphur bond acts as a link between metallic and organic systems, allowing for the thiol films to be used for example in biological sensing applications or as components in molecular electronics. Most of the modelling of these systems has so far been conducted using ab initio methods, mostly density functional theory (DFT). While DFT gives a great deal of information on the properties of the gold-thiol systems, it is very limited when it comes to simulating large systems and extended time scales. Some attempts to address this problem have been made using potential energy surface expressions for thiol films [2,3] and by combining reactive and non-reactive force fields.[4] Development of a fully reactive set of interatomic potentials for the entire AuSCH system would thus be very desirable. To this end, we have recently developed a potential for gold [5] in the ReaxFF framework. The ReaxFF framework is an attractive basis for developing the entire set of interactions as it already contains potentials for hydrocarbons and can also treat Coulomb interactions. In addition to presenting the gold potential, we show preliminary results obtained with the AuSCH model.

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Structural and Electronic Characteristics of Group 15 Elemental Nanotubes

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Abstract

Group 15 elements phosphorus, arsenic, antimony, and bismuth are all known to appear as layered materials. The layered bulk materials are composed of sheets of puckered six-membered rings, being structurally related to graphite. In analogy to the structural relationship between the single layers of graphite and carbon nanotubes, the individual sheets of the layered group 15 materials can be rolled into single-walled nanotubes.

We have investigated the structural and electronic characteristics of single-walled nanotubes composed of group 15 elements P, As, Sb, and Bi. Systematic quantum chemical studies on the elemental nanostructures were performed to obtain periodic trends for their stabilities, structural principles, and electronic properties. The structures and stabilities of the studied group 15 nanotubes converge smoothly towards their experimental bulk counterparts. The electronic properties of the nanotubes were compared with bulk materials to obtain insights into their potential applications.

Structural and Electronic Characteristics of Perhydrogenated Carbon and Boron Nitride Nanotubes

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Abstract

Structural characteristics of perhydrogenated carbon and boron nitride nanotubes have been determined by periodic B3LYP calculations. Utilization of line group symmetries enabled the study of single-walled nanotubes several nanometres in diameter. Two families of nanotubes were systematically studied for both carbon and boron nitride: (1) the nanotubes derived from the hydrogenated (110) sheet and (2) the nanotubes derived from the (111) sheet of diamond and cubic boron nitride. Perhydrogenated carbon nanotubes prefer structures analogous to the hydrogenated diamond (111) sheet.[1,2] In clear contrast, the single-walled perhydrogenated boron nitride nanotubes prefer structures analogous to the (110) sheet.[2,3] The significantly different structural characteristics originate from polarization of the B-N bonds, resulting in polarized hydrogens and electrostatic interactions between them. As a consequence, multilayering is beneficial for perhydrogenated boron nitride sheets and nanotubes due to attractive electrostatic H-H interactions between layers. The structural characteristics of the perhydrogenated CNTs and BNNTs apply for heavier group-14 hydrides and group 13-15 binary hydrides. Perhydrogenated group-14 nanotubes prefer (111) structures, group 13-15 nanotubes having more diverse structural characteristics due to the electrostatic H-H interactions.

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Optical Properties of Silicon Nanoclusters

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Abstract

Light emitting silicon nanoclusters have been studied extensively during recent years. However, the actual mechanism responsible for the strong optical activity of the nanoclusters has remained unsolved. We have studied free-standing silicon nanoclusters with hydrogen terminated surfaces and their electronic excitations up to Si329H196 using time-dependent density functional theory. Different types of oxygen defects were also investigated. The computed excitation energies are often in good agreement with the experimental observations, but the oscillator strengths of the transitions are usually significantly smaller than reported in experiments. We have also proposed a new class of silicon nanoclusters with silane modified surface, which have both energies and oscillator strengths in accordance with experiments, as possible candidates for strongly luminescent silicon nanoclusters.

Calculation of electrostatic potentials for biomolecules using a tensorial finite-element approach

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An accurate description of electrostatic potentials (ESP) is fundamental for modelling biological processes. The "Direct Approach to Gravitation and Electrostatics" algorithm [1, 2] is a fast, massively parallelizable, and accurate means for determining ESPs from charge densities obtained from quantum chemical calculations. Contrary to traditional Poisson solvers, the present finite-element approach employs tensorial element functions, and thus does not need any knowledge of the boundary conditions of the potential; the ESP is obtained by efficient numerical integration of the Coulomb interaction. We focus here on the respiratory mechanism of cytochrome *c* oxidase (CcO) [3]. In this transmembrane enzyme, the electron transfer takes place between four redox-active metal centers: $\mathrm{Cu_A}$, heme *a*, heme a_3, and $\mathrm{Cu_B}$ groups. The changes in charge density due to the electron transfer direct protons either to the binuclear heme $a_3/\mathrm{Cu_B}$ site, where O_2 is reduced to H_2O, or to be pumped across the membrane. Accurate calculations of the ESP at the active site are expected to yield better understanding of the proton transfer mechanism of CcO.

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DFT and ab-initio study of dihydrogen interaction with new lithiated organic linkers suitable for hydrogen storage applications

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Abstract

By means of DFT and ab-initio calculations, the interaction energies between H2 and three new lithiated organic linkers are calculated. The benzene derivates studied in this work are lithium benzide (C6H5-Li), lithium phenolate (C6-H5-OLi) and lithium benzoate (C6H5-COOLi). The computational techniques applied in this work range from Density Functional Theory (DFT), to second-order Møller-Plesset perturbation theory (MP2) and coupled-cluster theory including all single and double excitations in conjunction with a perturbative estimate of triple excitations [CCSD(T)]. By extrapolating the MP2 and CCSD(T) energies to the complete basis set, the interaction energy of dihydrogen with these benzene species is found to be 2.5, 2.7 and 2.6 kcal/mol respectively. Furthermore, the lithium benzide and lithium phenolate may absorb up to 7 dihydrogens with mean interaction energies of 2.1 and 2.0 kcal/mol per H2. Therefore, these organolithium structures can be used as building blocks for hydrogen storage applications.

Adsorption of simple hydrocarbons on palladium surface – the role of subsurface carbon

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Abstract

It has been discovered in recent experimental studies that pure palladium surfaces are not responsible for selective hydrogenation of ethyne.[1] Instead the selectivity is provided by a metastable phase composed of palladium surface atoms and carbon impurities. The exact structure of the carbide hasn't been established, but the amount of carbon close to the surface has been defined to be 35 atomic. We have simulated the formation and composition of the subsurface C layer applaying DACAPO software[2] which is based on density functional theory (DFT). First we looked into C diffusion from the surface to the lattice. We found out that carbon adsorption to subsurface sites is more favourable from step sites than from terrace sites. We also studied the diffusion within the lattice and our results agreed well with earlier theoretical and experimental works.[3,4] To study the significance of the amount of carbon, we used two different models with carbon contents of 25 and 33 atomic below the surface. These models were constructed with fcc(111) slabs containing six surface Pd atoms and two or three C atoms beneath the surface. The C atoms were positioned to interstitial sites between the first and second Pd layers from the surface. The structural differences between the most stable structures for these two models are drastic. With two C atoms the Pd lattice expands only a little however with three atoms the flat surface transforms to a sligthly stepped one. We studied binding of ethene and ethyne on the C modified surfaces. The surface with 25 atomic of C binded the adsorbates more weakly than a clean Pd surface whereas the surface with 33 atomic of C binded the adsorbates more strongly than a clean surface.

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Sign Preference and Nucleation

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Abstract

Nucleation on ions is an important process in the atmosphere. Ions of opposite sign have been observed to exhibit different nucleation rates as early as 1897 but the reason for this sign preference remained a mystery for more than a century. In a recent paper by Nadykto et al. (2006) it was demonstrated that the sign effect can be predicted by carrying out relatively simple quantum chemical calculations. The ion-induced component of atmospheric nucleation has been observed to be related predominantly to negative clusters. Since the role of sulfuric acid in atmospheric new-particle formation is thought to be very important, this negative sign preference can be chemically rationalized by assuming that sulfuric acid is the molecule responsible for the first steps of nucleation and showing that sulfuric acid exhibits a negative sign preference.

The binding of sulfuric acid to a series of anions and cations of varying chemical complexity was studied. Sulfuric acid is always bound more strongly to anions than to cations. This can be qualitatively explained using two rather simple structural and chemical concepts. First, the three-member S-O-H groups which form hydrogen bonds to anions are much more flexible than the two-member S=O groups which bond to cations. In effect, the S-O-H groups act as ?claws?, grabbing and holding on tightly to the anions. Second, sulfuric acid is a strong acid, and thus prefers to bind to anions, which usually have some degree of basic character. The specific chemical interactions may, in some cases, be far more important for ion-induced nucleation than general electrostatic effects.

Replication of known experimental results is an efficient way to test the limits and reliability of quantum chemical methods. The objective was to replicate the sign preference observed experimentally by Winkler et al. (2008). The intermediate results implicate a positive sign preference in contradiction with the experimental results. Furthermore, difficulties in modelling the cationic case were encountered. The exact reason for this is not clear. However, the limitations of quantum chemical methods set by limited computational resources may be an important factor in our case.

Calculation of magnetically induced current densities

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Abstract

A method for calculating magnetically induced current and spin densities using gauge-including atomic orbitals (GIAO) is presented.[1] The method has been implemented at the Hartree-Fock self-consistent-field (HF-SCF), density functional theory (DFT), and ab initio electron-correlated levels. The gauge-including magnetically induced current (GIMIC) method has been employed in studies on fullerenes,[2] aromatic hydrocarbon nanorings,[3] polycyclic antiaromatic hydrocarbons,[4] and metal clusters.[5] The method has also been used to assess the degree of aromaticity of Mbius aromatic molecules.[6] A scheme for obtaining quantitative values for the induced current strengths passing selected bonds in molecules via numerical integration over the current flow is presented. The obtained current susceptibilities can be used as a measure of the electron delocalization or molecular aromaticity.

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Variational calculations of the stretching and benging modes of the ammonia molecule adsorbed on Ni(111) surface

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Abstract

We have developed a six-dimensional variational program for ammonia-type molecules in order to model the vibrational frequencies of the ammonia molecule adsorbed on Ni(111) surface and on other metal surfaces. Vibrational potential energy surfaces have been obtained from *ab initio* calculations using plane-wave density functional theory with periodic slabs modeling the metal surface as implemented in the Vienna *ab initio* simulation package (VASP). Six-dimensional variational calculations are an extension to our previous work where the stretching modes of ammonia adsorbed on Ni(111) have been computed using a local mode model for anharmonic N-H bond oscillators.[1]

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Experimental and Theoretical Analysis of Asymmetric Induction in Heterogeneous Catalysis: Diastereoselective Hydrogenation of Chiral α-Hydroxyketones over Pt Catalyst

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Abstract

Accessing the origin of asymmetric induction in heterogeneous hydrogenation is a challenging task. In this work, hydrogenation of a chiral compound, (*R*)-1-hydroxy-1-phenyl-2-propanone [(*R*)-PAC], in toluene over cinchonidine modified and unmodified Pt/Al_2O_3 was studied. In order to reveal the detailed reaction mechanism and the origin of stereoselectivity in the Pt catalyzed hydrogenation of the C=O double bond, the structures and energies of several adsorption modes of (*R*)-PAC as well as whole reaction paths for hydrogenation were investigated on Pt(111) by density functional theory (DFT). In agreement with experimental results, the theoretically obtained potential energy profiles for the studied hydrogenation mechanisms implied that (1*R*,2*S*)-1-phenyl-1,2-propanediol is formed in excess with respect to the other diastereomeric product diol, (1*R*,2*R*)-1-phenyl-1,2-propanediol. Pairwise addition of hydrogen was the most energetically favorable mechanism. Relative stabilities of the transition states of the *re*- and *si*-face hydrogenation elementary steps were similar to those of the corresponding stable intermediates. Adsorption and hydrogenation of other structurally similar chiral α-hydroxyketones, (*R*)-3-hydroxy-2-butanone and (*R*)-2-hydroxy-1-cyclohexanone, were also studied computationally on Pt(111). The results showed that cluster model DFT calculations can be used to assess (dia)stereoselectivity in metal catalyzed hydrogenation of even such complex organic molecules as studied here.

Chromatographical techniques for defining chemical components of metabolites of microscopic fungi destroying metals

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Abstract

Organic acids produced by micromycetes play double role: on the first hand they form agressive environment and on the other hand they serve as an extra carbon sources for growing microorganisms.

As an objects for research we used such metals as magnium, aluminium and zinc, which we put into inoculated Petri cups. After exposition products including products of biocorrosion and metabiolites of microorganisms were mechanically eliminated from the surface. Then for separating ekzometabolites products were combined with 0,2M HCL and then evaporated. Analysis were held using HPLC with spectrophotometric detector (250 nm).

Kinetic Properties of Vacancy-Type Defects and Adatoms (H, O) on Graphene and Carbon Nanotube

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Abstract

It has been shown that defects can essentially change the properties of graphene and carbon nanotubes. In particular, such defects as vacancies (V, V2) and adatoms (H, O) has attracted much attention as those most often created during the growth and experimental treatments. In order to be able to predict their influence on the properties of the graphene/nanotube, one has to know their kinetic behaviour on its surface including cases when defects interact with each other. However, for the most of the mentioned defects only the information about their adsorption and, for some complexes, binding energy are available in the literature. The data on diffusion characteristics of the defects and their complexes is scare. In this work we study kinetic properties of vacancies and adatoms (H, O, OH) on graphene and carbon nanotubes. For this purpose we have calculated vacancy-vacancy, vacancy-adatom and adatom-adatom interaction potentials and their diffusion parameters using first principle density-functional methods. The analysis of probable defect microstructure of graphene and carbon nanotubes and their electronic properties are discussed.