

Ta Clusters on Amorphous Silica: DFT Calculations Reveal a Notable Flexibility of the Support

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Introduction

Small Ta clusters on amorphous silica have been synthesized from $\text{Ta}(\text{CH}_3)_5$ at elevated temperatures under a hydrogen atmosphere [1]. EXAFS results were assigned to adsorbed clusters assigned as Ta_3 , with Ta-Ta distances of 289 pm and two different Ta-O distances, 189 and 199 pm. The aim of our density functional study was to identify possible structures and ligand compositions of the adsorbed clusters from scalar relativistic all-electron calculations, and, using periodic plane-wave calculations, to explore the changes induced by the Ta species in the silica support.

Materials and Methods

Periodic supercell calculations were carried out with the plane-wave based Vienna ab initio simulation package VASP [2], using the gradient-corrected exchange-correlation functional PW91. The ideal (111) surface of β -cristobalite was described by an infinitely extended, ideal slab model comprising three Si layers, each of which contained eight Si atoms in the unit cell. Dangling bonds were at the boundaries of the model slab were saturated by H atoms, except at the adsorption site (on one side). The repeated slabs were separated by a vacuum spacing of at least 1 nm to minimize spurious interactions. The "bottom" layer of each slab was kept fixed at the calculated bulk-terminated geometry; the two upper layers were allowed to relax during geometry optimizations, together with the adsorbate.

Cluster calculations were carried out with our parallel density functional program PARAGAUSS using the linear combination of Gaussian-type orbitals fitting functions density functional method at the all electron level [3]. To account for the Ta atoms we used the scalar relativistic variant of the LCGTO-FF-DF method which employs a second-order Douglas-Kroll-Hess method to solve the Dirac-Kohn-Sham problem. We employed the hybrid QM/MM approach covEPE to describe the interaction of a finite QM model with its extended environment in a self-consistent fashion [4].

Results and Discussion

Ta_3 species likely interact with at least three (mostly non-bridging) oxygen centers of the surface. Interaction with hydroxyl groups was calculated too weak. Comparison of EXAFS data for Ta_3 species to results of DFT calculations provides evidence for H-ligation of the Ta species. Models of adsorption complexes with a single Ta-O contact were unable to reproduce the experimental Ta-Ta distances of ~290 pm.

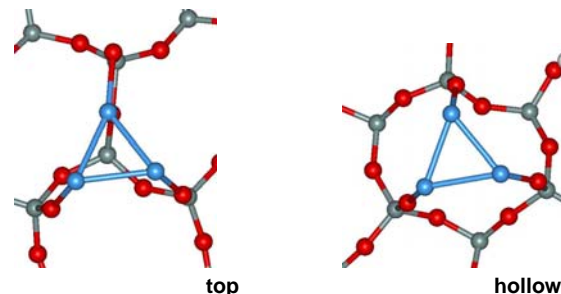


Figure 1

Schematic representation of two types of adsorption sites of Ta_3H_n clusters on the (111) surface of β -cristobalite, viewed from above along the (111) direction.

We considered two different adsorption sites for slab models of Ta_3H_n on the (111) surface of β -cristobalite (Fig. 1): adsorption (1) "on top", where the Ta_3 group sits above a Si tetrahedron and (2) with hollow coordination, over the center of a SiO_2 framework ring. The "top" site, where bare Ta_3 cluster interacts with 4 O atoms, is slightly more stable, by 9 kJ/mol, than the complex with hollow coordination. For the latter, we determined two local equilibrium structures of Ta_3 : one with 5 Ta-O contacts, the other one with 3 such contacts. With $n > 3$ in supported Ta_3H_n clusters, the two bridging O centers of the 5 Ta-O contacts disappear. We found a rather high hydrogen loading n . Average energies of dissociative adsorption were ~100 kJ/mol per H for $n = 3$ and decrease slowly for higher loadings, e.g. to ~75 kJ/mol per H for $n = 10$. The support reacts rather strongly to adsorption of Ta_3H_n . O centers closest to the adsorbed cluster are attracted strongest. These centers shift typically by 40–100 pm. Neighboring Si centers are displaced by up to 20 pm, while the O centers which are far away from the adsorbed cluster shifted by 15–25 pm. In slab models bare Ta_3 clusters occasionally interact with bridging oxygen centers.

Significance

Small Ta particles catalyze several important reactions, such as hydrocarbon framework rearrangements, synthesis of aromatic species; they also dissociate dinitrogen [1,5]. Because of that versatile ability to catalyze key reactions it is worthwhile to study the actual surface species generated and their interaction with the support.

References

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