Surface Science 652 (2016) 278–285

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Predicting catalyst-support interactions between metal nanoparticles and amorphous silica supports

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ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form 26 February 2016
Accepted 3 March 2016
Available online 10 March 2016

Keywords:
Metal-support interaction
Amorphous silica
Density functional theory
Catalysis

ABSTRACT

Metal-support interactions significantly affect the stability and activity of supported catalytic nanoparticles (NPs), yet there is no simple and reliable method for estimating NP-support interactions, especially for amorphous supports. We present an approach for rapid prediction of catalyst-support interactions between Pt NPs and amorphous silica supports for NPs of various sizes and shapes. We use density functional theory calculations of 13 atom Pt clusters on model amorphous silica supports to determine linear correlations relating catalyst properties to NP-support interactions. We show that these correlations can be combined with fast discrete element method simulations to predict adhesion energy and NP net charge for NPs of larger sizes and different shapes. Furthermore, we demonstrate that this approach can be successfully transferred to Pd, Au, Ni, and Fe NPs. This approach can be used to quickly screen stability and net charge transfer and leads to a better fundamental understanding of catalyst-support interactions.

1. Introduction

This paper is dedicated to the memory of our dear friend and mentor, John T. Yates, Jr. His wide-ranging interests, keen scientific insights, wonderful sense of humor, and compassionate humanity made him a delight to talk with. He is greatly missed.

Control over nanoparticle (NP) catalyst-support interactions may offer a handle for tuning catalytic properties such as activity and stability. However, despite advancements both in computational [1–7] and experimental techniques [8–10], prediction of catalyst-support interactions can be daunting. As research has begun to shift towards ever more complex support materials, such as transition metal doped oxides [11,12], the development of capabilities to model support effects is becoming increasingly important. Yet, despite significant progress in atomistic modeling methods, explicit inclusion of support effects remains a challenge [6,7].

Amorphous silica is a commonly used catalyst support due to its good thermal stability as well as tunable porosity and surface area [13, 14]. Additionally, the chemical and physical properties of silica can be further controlled via doping with transition metals such as Ti, making silica an attractive platform for tuning catalyst-support interactions. Prediction of support effects of amorphous surfaces, however, requires calculation of a broad distribution of catalyst-support interactions because amorphous supports exhibit a range of local surface structures.

We recently developed an approach for rapid prediction of NP-support interactions between platinum and amorphous silica [15]. We used density functional theory (DFT) calculations to discover linear correlations for the adhesion energy and net charge on a NP as a function of the NP size and hydroxyl density of the silica support for a small set of Pt NPs [15]. We demonstrated that these correlations can be used to predict adhesion energies and charges for other Pt NPs through the use of fast discrete element method (DEM) simulations to predict the number of Pt-silica bonds [16]. Here, we extend our approach to NPs with different shapes and compositions. Specifically, we demonstrate that (a) correlations obtained for 13-atom Pt clusters are valid for NPs of larger sizes and different NP geometries, and (b) this approach can be successfully applied to other catalytic metals such as Pd, Au, Ni, and Fe NPs.

2. Method

2.1. Model amorphous silica surfaces

Our calculations are based on the amorphous silica structures developed by Ewing et al. [17] to investigate NP-surface interactions. These model surface structures are derived from first-principles simulations and have been shown to accurately predict hydroxyl density and the distribution of hydroxyl groups as a function of temperature without any adjustable parameters. Five model surfaces were generated and the hydroxyl density of each system was adjusted using an algorithm that simulates a range of silica pretreatment temperatures T_{pre}, resulting

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http://dx.doi.org/10.1016/j.susc.2016.03.004
0039-6028/

in a total of 56 different surface structures. For the DFT calculations in this work, we use two of these surface structures having alternatively high (4.5 nm^{-2}) and low (1.6 nm^{-2}) hydroxyl densities, corresponding to low (200 °C) and high (570 °C) T_{pre}, respectively. For the discrete element method (DEM) calculations described below we use all 56 surface structures. Details of unit cell dimensions and system sizes can be found in the Supporting Information.

2.2. Metal nanoparticles

For the majority of calculations in the present study we used magic number cuboctahedral NPs because the symmetry is independent of size. To investigate the effects of NP geometry on the catalyst-support interactions we also used the calculated gas-phase global minimum configuration for Pt_{13} ("opt"), and "slab" geometries for Pt_{55} and Pt_{147} (elongated in the *y* dimension; 3 atomic layers thick). All NP geometries used in this study are shown in Fig. 1. To calculate the dependence of several electronic structure properties on the element identity, we used 13-atom cuboctahedral NPs of Au, Pd, Fe, and Ni, as well as 147-atom cuboctahedral NPs of Au and Pd.

2.3. Simulating NP adsorption

We divided each silica surface into grids to sample different adsorption locations on the surface. In our DFT calculations, silica surfaces for 13-, 55-, and 147-atom NPs (of a given composition, geometry, and orientation) were typically divided into grids of 9 (3 × 3), 9 (3 × 3) and 6 (3 × 2) adsorption locations (in the *xy* plane), respectively. To demonstrate the use of our approach for comparing the stability and net charge of different NP shapes and sizes, we performed additional DEM simulations for all Pt NPs. For all of these DEM simulations, we divided each silica surface into grids of 80 (10 × 8) adsorption locations. Specific details about the division of cells into grid points are provided in the Supporting Information.

We simulated the adsorption of NPs onto the silica surface using discrete element method simulations followed by DFT calculations, as described in detail previously [15,16]. The DEM simulations were used to generate reasonable initial structures for the placement of NPs on the silica surface and to compute an estimate for the number of metal-silica bonds. For the purpose of our study, the forces in DEM were limited to only gravity, tangential friction, and viscoelastically-damped hard-sphere interactions where rebounding of particles (atoms) is completely avoided by tuning the viscoelasticity of the particles in the simulations. It is known experimentally that Pt and Pd metal NPs supported on silica typically form bonds between the metal (M) and silica surface through Si–O–M linkages [18–20]. It is known that Si–M bonds are more energetically favorable than Si–O–M linkages, e.g., as has been shown for silica-supported Au NPs [21,22]. However, Si–M bonds typically are kinetically limited to forming at high temperatures [18–20] and therefore we restrict our calculations to metal–oxygen bonding in the present work because we assume that cleaving the O–H bond in order to form the Si–O–M linkage is kinetically favored. Furthermore, in a previous study we found that Pt–O bond formation is energetically favorable for Pt/silica. We found that H migration from silanol to a Pt_{13} cluster accompanied by a Pt–O bond formation resulted in ~2.4 eV reduction in system energy [15,16]. We model M–O bond formation by creating bonds between the NP and any surface hydroxyls that are in contact with metal atoms in the NP by removing the H atom from those hydroxyl groups and reducing the hard-sphere interactions between the interacting M and O atoms to their covalent rather than van der Waals (vdW) radii. The DEM-initialized geometries were fully relaxed to their local minima using DFT for a select group of systems. In addition, many other NP structures were generated on each of the 56 silica surface structures using DEM in order to gain a more complete picture of the number of metal–silica bonds as a function of NP size and geometry (see below).

2.4. Density functional theory calculations

All DFT calculations performed in this work used the CP2K code, which employs a Quickstep [23] implementation of the DFT method using a combination of plane waves and pseudopotentials with localized Gaussian basis sets (see Supporting Information for details). We used the revised PBE functional (revPBE) [24] and GTH pseudopotentials [25,26] in conjunction with short range double-ζ basis sets with polarization functions (SR-DZVP) [27] in our calculations. vdW interactions were included using the DFT-D3 method [28]. All surface slabs were relaxed using CP2K with supercells that were periodic in all directions with at least 20 Å of vacuum between periodic images in the *z* dimension to mitigate interactions between the periodic images of the surface slabs. The parameters for plane wave energy cutoff, basis sets, vacuum spacing and spin-restricted relaxation used are shown in the Supporting Information and have been validated for these systems previously [16]. The *xy* dimensions of the periodic surface slab for each NP size were previously shown to be sufficient to avoid significant error due to self-interaction of the NP with its periodic image [16].

2.5. Calculating nanoparticle properties

NP adhesion energy and net charge are primary components of this study. We approximate the adhesion energy as the energy necessary to instantaneously pull the NP from the support surface. Deformation energies for these systems have been shown to be small enough that they do not affect the general trends of adhesion energy versus the

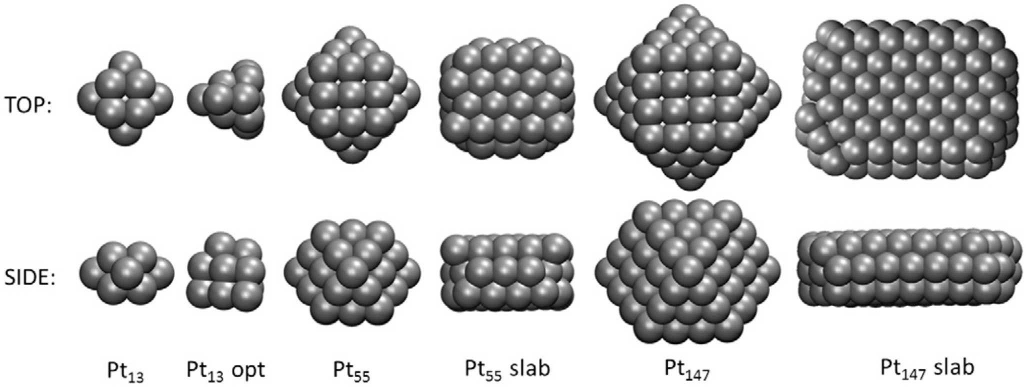

Fig. 1. Top and side views of the NP geometries used in this study, from left to right: cuboctahedral Pt_{13}, theoretical gas phase global minimum Pt_{13}, cuboctahedral Pt_{55}, slab Pt_{55}, cuboctahedral Pt_{147}, and slab Pt_{147}.