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# Geometry of the Adsorption Sites in Metal Nanoparticles and Surfaces †

**Constantinos D. Zeinalipour-Yazdi**

Bioscience and Chemistry, Faculty of Computing, Mathematics, Engineering and Natural Sciences, Northeastern University London, London E1W 1LP, UK; c.zeinalipouryazti@northeastern.edu or constantinos.zeinalipour@nulondon.ac.uk

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**Abstract**

Despite decades of surface science research, there is a lack of an universal approach to define the adsorption geometry in catalysis on metal nanoparticles and surfaces. The unified framework introduced in this work allows the comparison of binding sites across different facets and particle-size metals, including stepped surfaces, adatoms and surface vacancies. In this study, we identify 18 adsorption sites on metal nanoparticles and surfaces that have either a face-centred cubic (FCC) or hexagonal close-packed (HCP) structure. Most metals in the periodic table have these structures and we determined the adsorption site geometry on a nanoparticle using a geometric approach with physical magnetic ball-and-stick models. These geometric models include the existence of an octahedral or tetrahedral hole beneath the adsorption site, as these can affect the adsorption site strengths of adsorbates. Furthermore, these adsorption sites are a combination of three-fold hollows and four-fold hollows, which are adsorption sites known to activate diatomic molecules (e.g., $N_2$ and CO). In addition, adsorption of large-molecular-weight adsorbates can be defined on these sites as they provide multiple contact points in contrast to the typical four-fold hollow, three-fold hollow, and bridge and atop adsorption sites used in heterogeneous catalysis. We find that there are nine geometrically distinct adsorption site topologies composed of square (i.e., 100) and triangular (i.e., 111) motifs. These adsorption site topologies, when combined with a characteristic zeta angle ($\zeta$), result in 18 distinct adsorption site geometries that can be found on metal nanoparticles and surfaces. A systematic naming system for these adsorption sites is provided that defines the adsorption site geometry explicitly. Using this approach, we find that there are five different types of B5 sites, an adsorption site that has been previously found to activate dinitrogen on ruthenium for the ammonia synthesis reaction.

**Keywords:** geometry; HCP; FCC; adsorption site; magnetic ball-and-stick models; ammonia synthe-sis; B5 site

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## 1. Introduction

Physical molecular models are used mainly in chemistry and materials science education but can also be used in catalysis research. In this study, the various adsorption site topologies on metal nanoparticles (NPs) and metal surfaces of hexagonal close-packed (HCP) and face-centred cubic (FCC) metals have been identified and geometrically analyzed.

The analysis with physical magnetic ball-and-stick molecular models demonstrates that the adsorption site geometry can be fully described by triangular- or square-atom motifs that are either bridge or are atop-bound, with additional labels that indicate whether the local site is on top of a tetrahedral or octahedral hole and a characteristic zeta angle ($\zeta$) between the square (i.e., four-fold hollow) and equilateral triangle (i.e., three-fold hollow) geometric shapes.

With this theoretical approach, we find that there are nine adsorption site topologies, 18 adsorption site geometries and five different b5-sites [1–4].

A simple nomenclature system for these adsorption sites and the corresponding geometry of the adsorption site is given, which can be readily applied in catalysis research to label the geometry of active catalytic sites and non-active adsorption sites on metal nanoparticles and surfaces.

## 2. Materials and Methods

We used magnetic ball-and-stick models (see Figure 1, Magnetic ball and rod set, China), trigonometry/geometry and photography to find the various possible geometries of adsorption sites on metal HCP and FCC nanoparticles. We first constructed the typical ABAB or ABCA stacking sequence and then removed atoms and the adjacent bonds from the surface of this nanocluster to reveal different adsorption site geometries, which were photographed in smaller, exact models of these adsorption site geometries similar to those found in a 60-atom magnetic ball-and-stick model. This primarily improved the visibility of the geometric shapes that construct these adsorption sites. All adsorption sites could be constructed by combining one or more octahedra, tetrahedra and square pyramids.

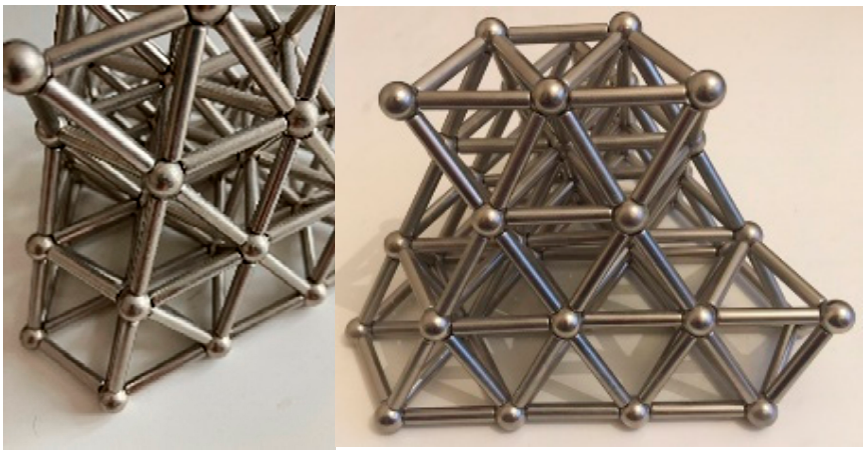

**Figure 1.** Magnetic ball-and-stick models. In these models, the stick is magnetic whereas the spheres are non-magnetic. These models can be readily used to construct ABAB and ABCA stacking of metals and other materials.

## 3. Results and Discussion

We then measured with a goniometer the characteristic dihedral angle between the different adsorption sites, and two examples of this are shown in Figure 2.

In Figure 3 the nine different adsorption site topologies are shown. We used a combination of two equilateral triangles (i.e., the three-fold hollow is denoted as **3f**) that are connected via a top atom labelled **t** and can be either on top of an octahedral hole (labelled **O**) or on top of a tetrahedral hole (labelled **T**), resulting in three geometric site topologies labelled **3f(T)-t-3f(T)**, **3f(O)-t-3f(T)** and **3f(O)-t-3f(O)**.

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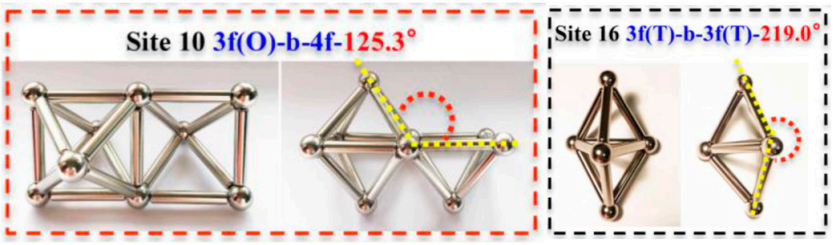


**Figure 2.** Magnetic ball-and-stick models. In these models, the stick is magnetic whereas the spheres are non-magnetic. These models can be used readily to construct ABAB and ABCA stacking of metals and other close-packed materials. Two local site geometries of HCP and FCC crystals (red dash) and HCP crystals (black dashed line). The red letters T and O correspond to tetrahedral and octahedral sites, respectively. The angle shown in red is the characteristic angle zeta (ζ). A complete list of the 18 adsorption sites can be found in Ref. [5].

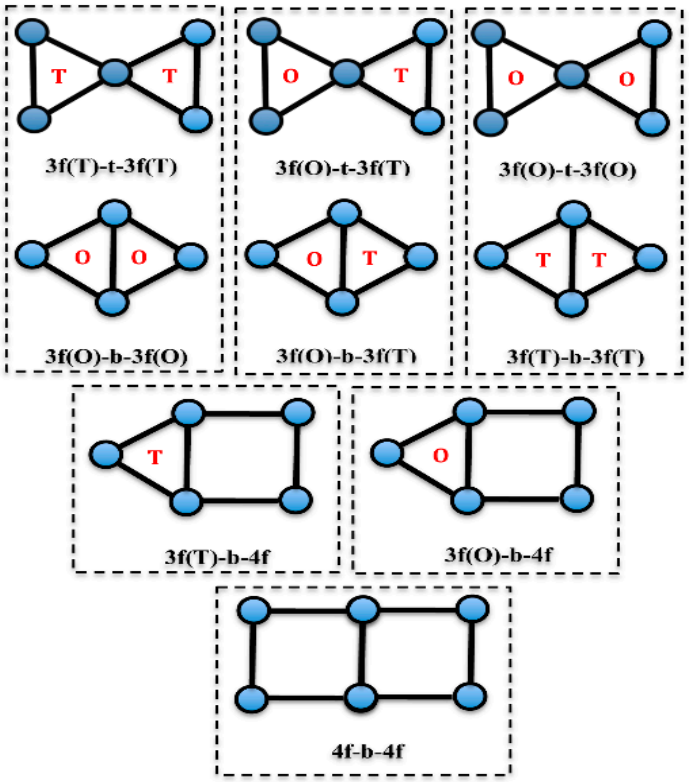


**Figure 3.** Magnetic ball-and-stick models. In these models, the stick is magnetic whereas the spheres are non-magnetic. This model can be used readily to construct ABAB and ABCA stacking of metals and other materials.

In these structures, two equilateral triangles can combine via a bridge site denoted as **b**. These combinations of three-fold hollow sites result in another three geometric site topologies labelled **3f(T)-b-3f(T)**, **3f(O)-b-3f(T)** and **3f(O)-b-3f(O)**.

A combination of an equilateral triangle and a square (i.e., four-fold hollow denoted as **4f** results in two geometric site topologies labelled **3f(T)-b-4f** and **3f(O)-b-4f**, where the three-fold hollow is on top of a tetrahedral hole and an octahedral hole, respectively. These are two other distinct geometric site topologies found on HCP and FCC NPs.

A combination of two squares (i.e., 4-fold hollow denoted as **4f**) results in one geometric site topology labelled **4f-b-4f**. So there are nine geometrically distinct site topologies possible on FCC and HCP nanoparticles on the basis of the type of sites combined.

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Lastly, consideration of the dihedral angle between the two geometric shapes (i.e., three-fold hollow and four-fold hollow) results in **18 distinct adsorption site topologies** which can exist on nanoparticles and surfaces (i.e., steps, adatoms, and defects).

The mathematical basis of the characteristic zeta angle (ζ) was derived previously and is a linear combination of the base angle of a square and trigonal pyramid [5].

Figure 2 presents the smaller ball-and-stick models we constructed to reveal the geometric shapes that construct the adsorption sites in the larger 60-atom ball-and-stick model shown in Figure 1. Using these smaller fragments made it possible to measure the exact angle in certain surface topologies with the use of a goniometer and observe what basic geometric shapes (i.e., octahedron, tetrahedron, or square pyramid) construct the various adsorption sites.

This analysis revealed that the characteristic angle takes values that are linear combinations of two dihedral angles found in basic geometric shapes. These shapes are shown in Figure 4, and the characteristic angle zeta (ζ) is the dihedral angle between the base and the side of an equilateral square pyramid (θ) or an equilateral tetrahedron (ε). These are geometric shape motifs that are repeated in the crystal structure of HCP and FCC metals and have exact values from geometry, as shown in Figure 4.

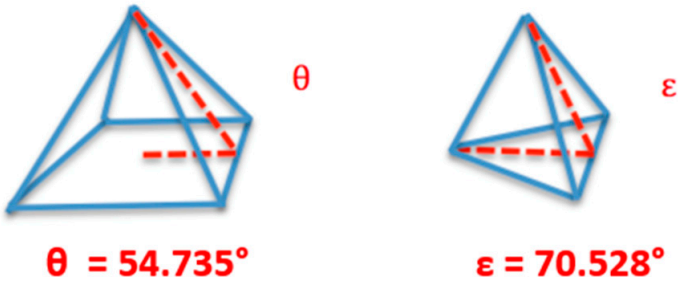


**Figure 4.** Base-to-side dihedral angle (shown with a red dashed line) in equilateral square pyramid and equilateral tetrahedron.

## 4. Significance

In catalysis, it is widely accepted that the exact geometry of the active site on nanocatalysts is an important parameter to model the kinetically favoured reaction mechanism. Certain reactions such as the ammonia synthesis reaction have higher turnover frequencies over B5 sites, which are primarily found for steps on iron nanoparticles. In this study, we find that nanoparticles that have HCP and FCC geometries but arbitrary surface terminations can have five B5 sites with a different zeta angle between the four-fold hollow and the three-fold hollow. We expect that this angle will have an effect on the activation of nitrogen, which is the rate-determining step of ammonia synthesis found on the iron catalyst. We also find that on small nanoparticles there is a plethora of adsorption site geometries for small molecules, with 18 different geometries that are distinct. These geometries have either:

a. A three-fold hollow next to a three-fold hollow;
b. A four-fold hollow next to a three-fold hollow;
c. A four-fold hollow next to a four-fold hollow.

In addition, the three-fold hollow can be either on top of an octahedral hole or on top of a tetrahedral hole, which results in nine adsorption site topologies. Considering the zeta angle between the two hollow sites, we found that there are 18 geometrically distinct adsorption site geometries on FCC and HCP metal nanoparticles and surfaces. It is conceivable that some of these adsorption site geometries are not catalytically active or have low reaction rates for a particular reaction mechanism.

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We provide a systematic naming convention of these 18 geometrically distinct adsorption sites, which are defined in analytical geometry and trigonometry and can be used as a general naming system for catalytic sites on FCC and HCP metal nanoparticles and surfaces. This geometric and mathematical analysis of adsorption sites found on metal catalysts will help classify reaction mechanisms from theoretical calculations and indicate which type of adsorption site is the kinetically fastest route for the reaction. This may have important implications in rational catalyst design in heterogeneous catalysis.

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**Data Availability Statement:** The data supporting this study and the mathematical derivation of the various adsorption site geometries is given in Ref. [5]. A poster of this conference proceeding at the 5th International Online Conference on Crystals (IOCC2026) can be found at the following link https://sciforum.net/manuscripts/31873/slides.pdf (accesed on the 5 July 2026).

**Conflicts of Interest:** The author declares no conflicts of interest.

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