

Geometry of the Adsorption Sites in Metal Nanoparticles and Surfaces

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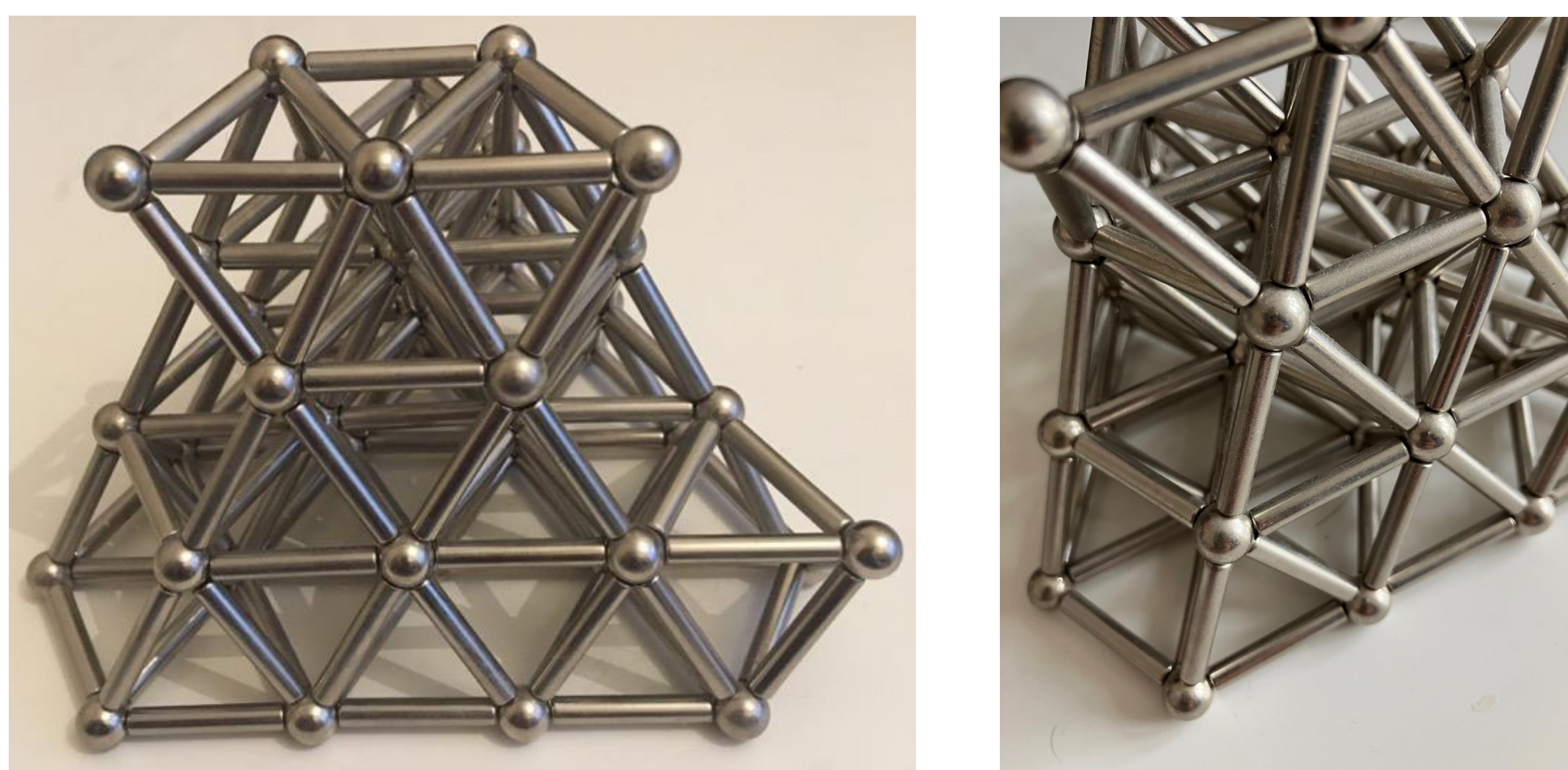
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INTRODUCTION & AIM

We present a study of 18 adsorption sites found on metal nanoparticles and surfaces that have either Face-Centred Cubic (FCC) or Hexagonal Close-Packed (HCP) structure. Most metals of the periodic table have these structures and we determine using a geometric approach the adsorption site geometry on a nanoparticle made using 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 the three-fold hollows and four-fold hollows that are adsorption sites known to activate diatomic molecules (e.g. N_2 , CO). In addition, adsorption of larger 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, bridge and atop adsorption. We find that there are 9 geometrically distinct adsorption site topologies that are composed of square (i.e. 100) and triangular (i.e. 111) motifs. These adsorption site topologies when combined with a characteristic angle (ζ) 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 explicitly the adsorption site geometry. Using this approach we find that there are five different type of B5 sites, an adsorption site that has been previously found to activate dinitrogen on ruthenium for the ammonia synthesis reaction.

METHODOLOGY

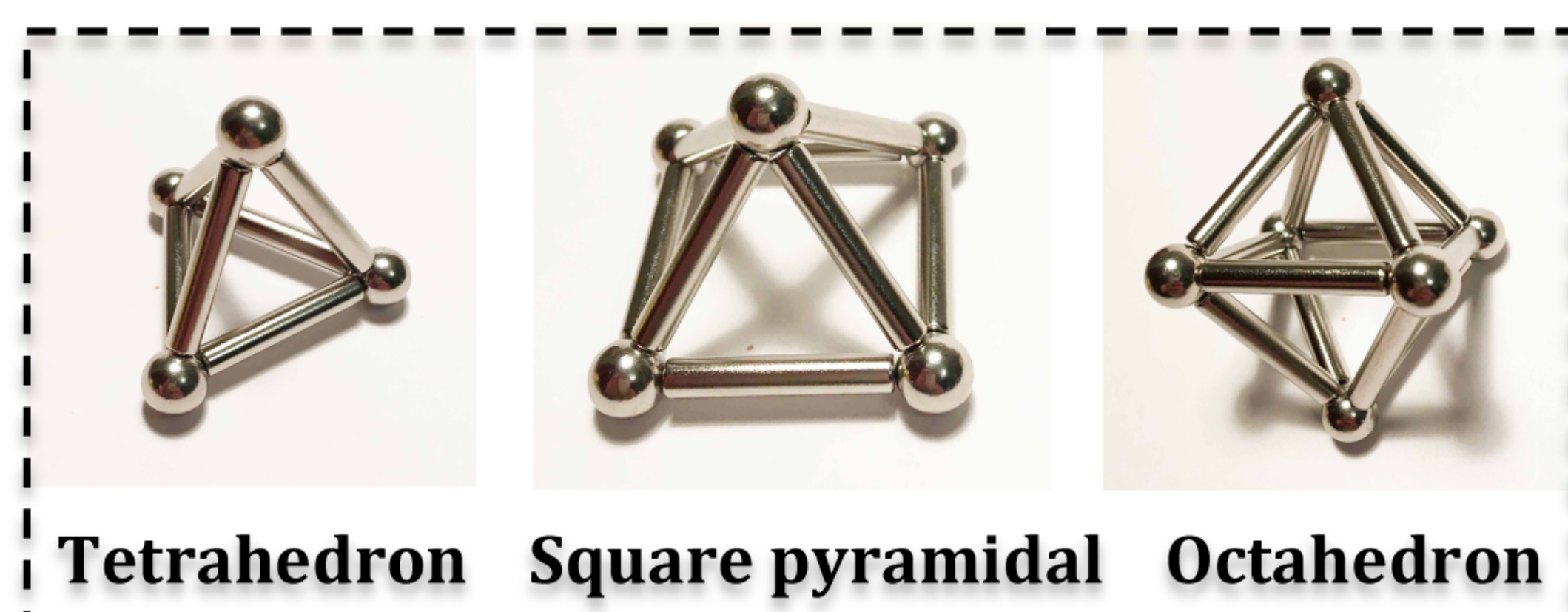
- We have used **magnetic ball-and-stick models** for this research
- The typical ABAB (HCP) and ABCA (FCC) stacking sequence of metal NPs was built and adsorption sites were photographed



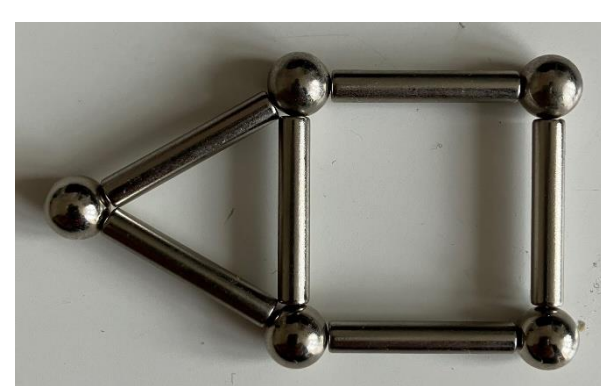
RESULTS - DISCUSSION

A. Basic geometric shapes in HCP and FCC crystals

- The **Hexagonal Close-packed (HCP)** and **Face-Centred Cubic (FCC)** structures have unit cells that can be composed of geometric shapes.
- These are two geometric shapes, the **tetrahedron** and **octahedron**, which define the tetrahedral (T) and octahedral (O) holes in the ABAB and ABCA lattices.



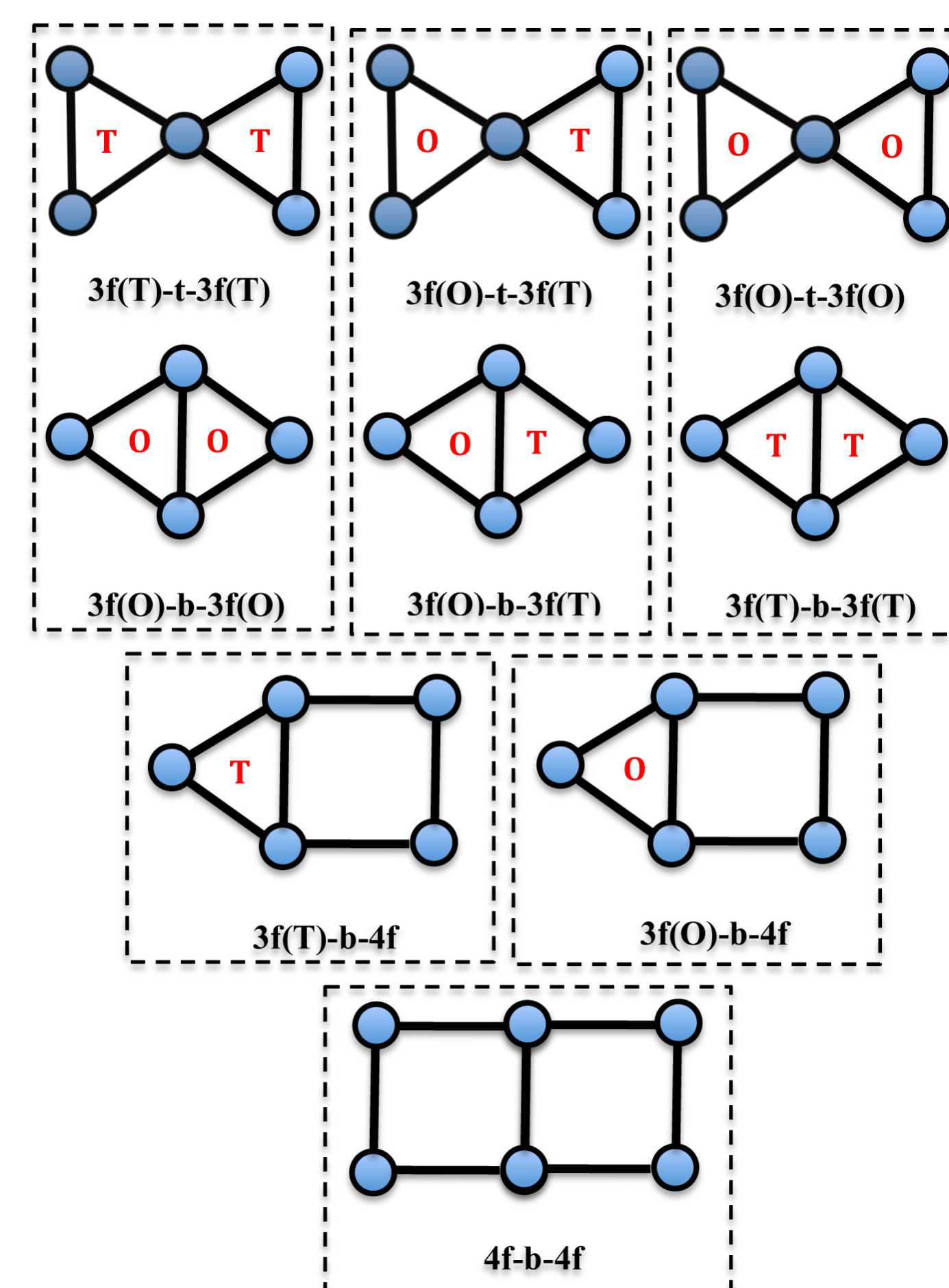
- Also the **square pyramidal** geometry appears at various surface terminations of the NP, such as along the (100) planes.
- Therefore, the **square** and **equilateral triangle** are the basic geometric shapes that appears on NP and surfaces



RESULTS - DISCUSSION

B. Adsorption Site Geometries on NP-based Catalyst Surfaces

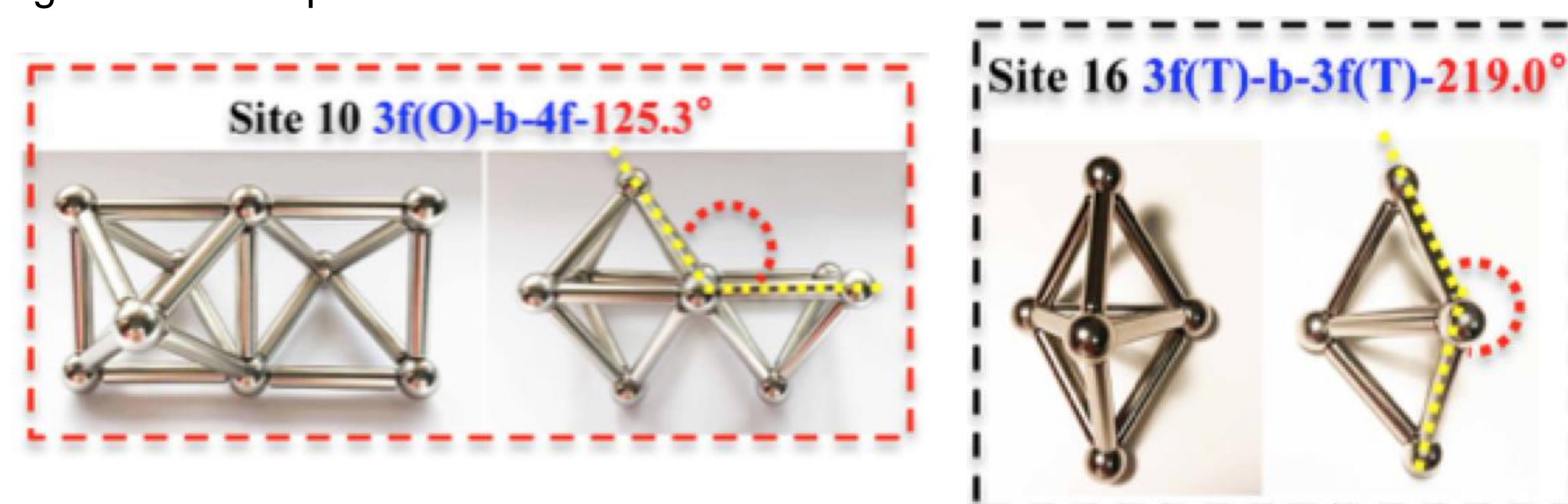
- Combination of two equilateral triangles results in **6 geometric site topologies**
 - Combination of an equilateral triangle and a square results in **2 surface topologies**
 - Combination of two squares in another **one**
- There are **9 geometrically distinct adsorption topologies** in HCP and FCC crystals



18 ADSORPTION SITE GEOMETRIES when the characteristic angle is defined

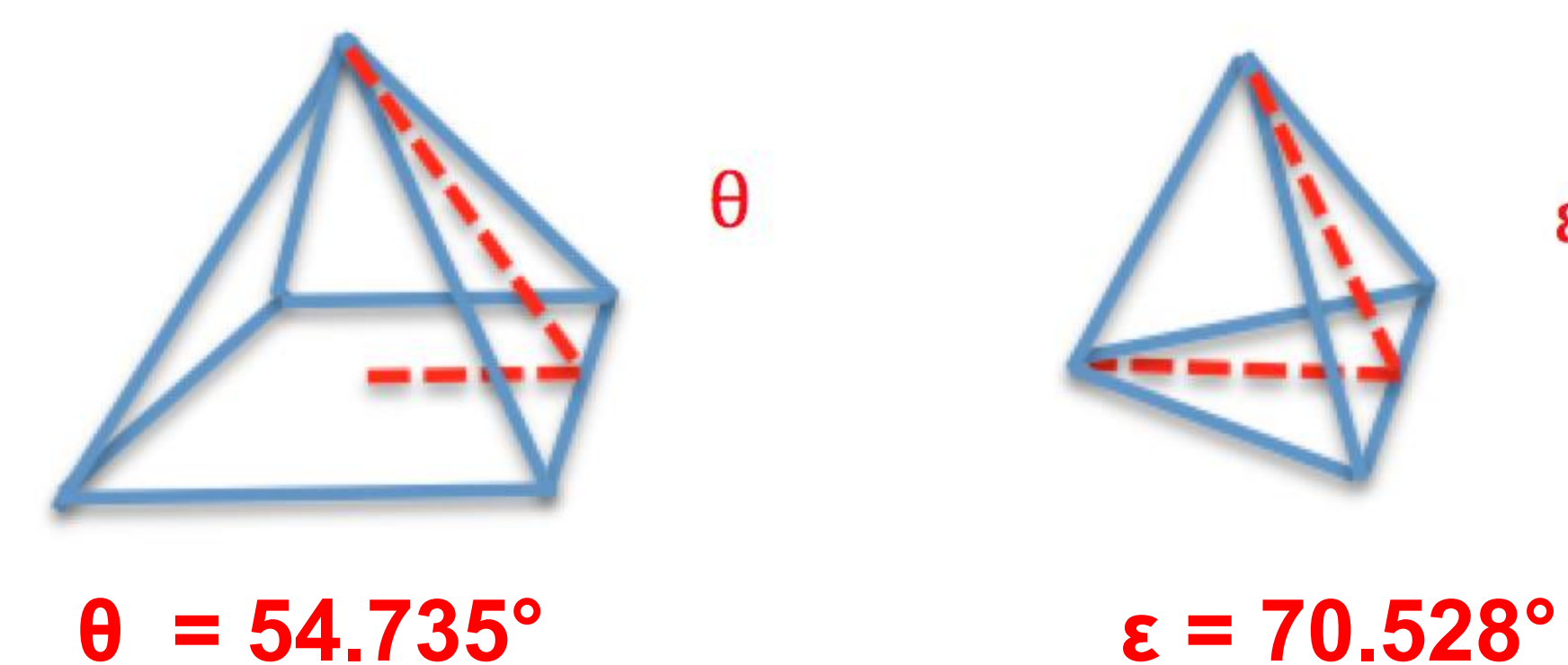
C. Adsorption Site Nomenclature System

- **3f(T)** stands for 3-fold hollow with a tetrahedral hole underneath
- **3f(O)** stands for 3-fold hollow with octahedral hole underneath
- **4f** stands for 4-fold hollow
- The triangles are connected either via a **t** (top) atom or via a **b** (bridge)
- There is a **characteristic angle (ζ)** that defines the angle between the two surface geometric shapes



D. What is the Geometric Basis of the Characteristic Angle

It is a linear combination of θ and ϵ dihedral angles of a square pyramid and tetrahedron



CONCLUSIONS

- We have used magnetic molecular models to study the adsorption site geometry in HCP and FCC NP and surfaces.
- We found 9 geometrically distinct adsorption topologies and 18 adsorption site geometries in HCP and FCC metals.
- Several of these adsorption sites may be within a nm on a NP.
- We provide a simple naming system of all possible adsorption sites and find that there are actually five different B5 sites possible on FCC and HCP metal nanoparticles and surfaces.

REFERENCES

Zeinalipour-Yazdi, C.D., Topology of active site geometries in HCP and FCC nanoparticles and surfaces, *Chem. Phys.* **2022**, *559*, 111532.