Supporting Information

Why Copper Catalyzes Electrochemical Reduction of Nitrate to Ammonia

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DFT convergence tests

Convergence tests on vacuum size and slab thickness were carried out to assess the efficiency and precision of various slab models. The best model is the smallest slab with the least amount of vacuum while still producing consistent results. Calculations are thus faster without compromising accuracy.

1- Vacuum size

A periodic unit cell in three dimensions is used to model our surfaces. This implies that even if vacuum is applied in the z-direction, the slab may still interact with itself. One method for accounting for artificial self-interaction is to apply a dipolar correction on the z-axis, which corrects potentials and forces acting on the slab. The other method is to ensure that the vacuum size is large enough to prevent slabs from interacting.

As show in Figure S1, all slab models deviate less than 8 meV compared to the 22 Å slab model, showing that the slab self-interaction is negligible even for the 16 Å slab model.

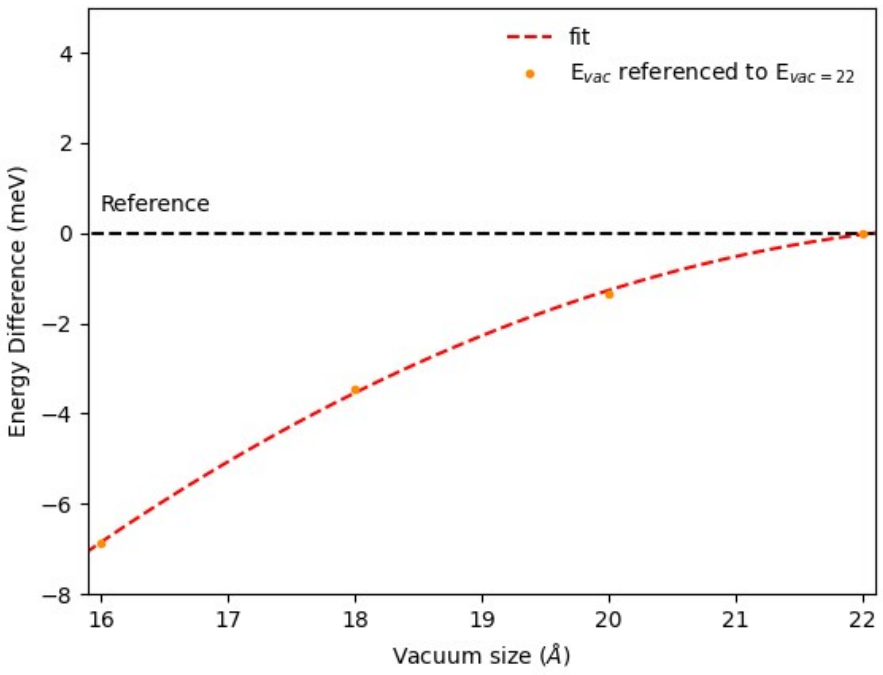

Figure S1. Electronic energy difference of slabs with a given vacuum size with respect to a slab with vacuum size of 22 Å.

2- Slab thickness and surface energy

In our next convergence test we investigated the surface energy and reaction energy differences for different slab thickness.

Surface energy calculations were done using the following equation:

$$\gamma = \frac{E_{Slab} - nE_{Bulk}}{2A},$$

where E_{Slab} denotes the electronic energy of the slab model, E_{Bulk} is the electronic energy of the bulk structure, n is the number of surface atoms per bulk atoms, A is the surface area and the factor of two arises due to having two surfaces, one located at the top side and the other at the bottom. Figure S2 shows that the surface energy remains the same regardless of the number of layers and how many bulk bottom layers are frozen.

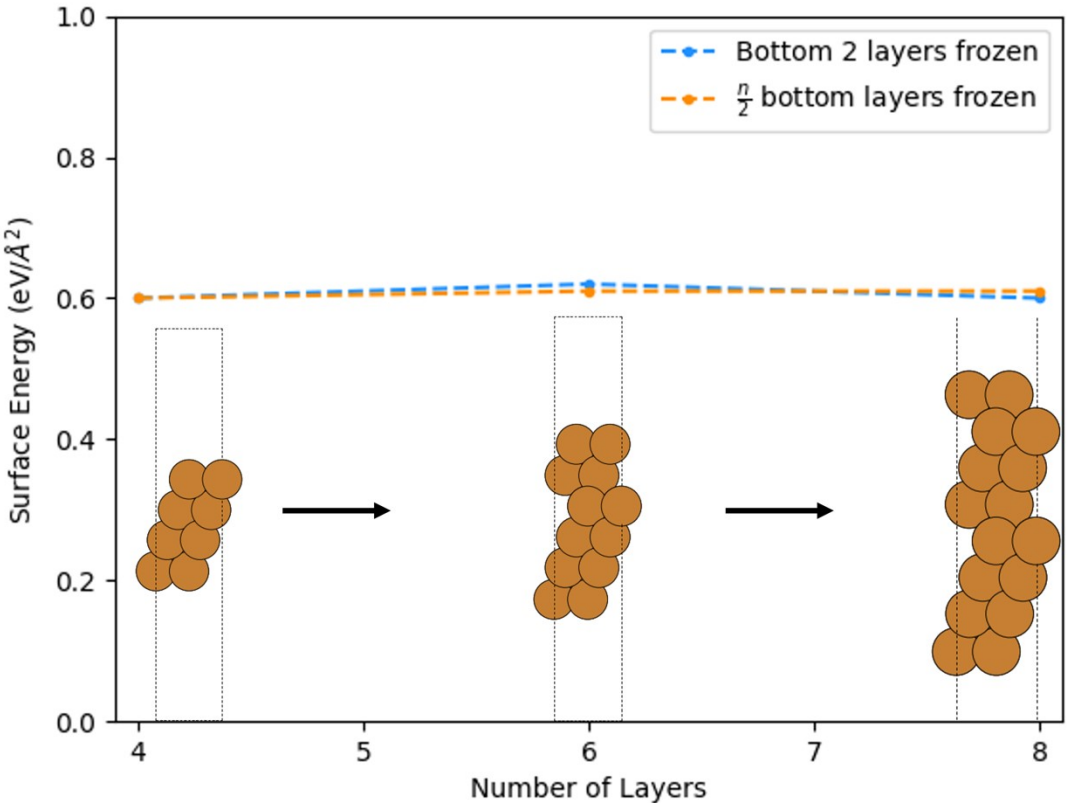

Figure S2. Surface energy of slab models with different number of layers.

3- Slab thickness and adsorption energy

To evaluate the impact of the thickness of our slab models in adsorption/reaction energies, we investigated the adsorption energy of NO_2 (Figure S3). The energy difference of the 4-layer slab

is slightly above 0.1 eV compared to the 8-layer thick. This demonstrates that 4-layer thick slabs may be insufficient to accurately describe adsorption/reaction energies; however, the overall quality of the reaction mechanism is unaffected because reaction energies will most likely offset by the same amount as observed in our convergence tests (4 layers compared to 6 and 8). Regardless, it has proven to be a powerful tool for gaining a qualitative understanding of the underlying reaction mechanisms and studying trends among various transition metals.

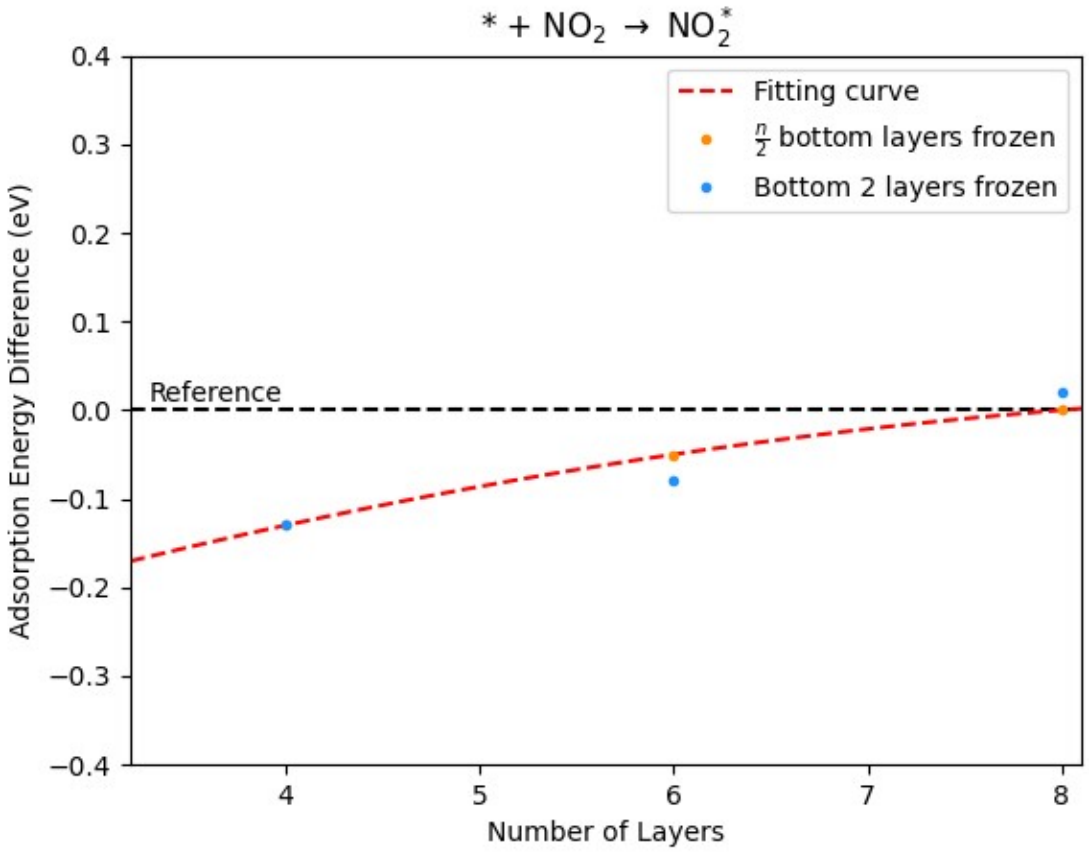

Figure S3. Adsorption energy difference of NO_2 referenced to the adsorption energy of the molecule in an 8-layer thick slab.