

## Supporting Information

### Controlling the Shapes of Nanoparticles by Dopant-Induced Enhancement of Chemisorption and Catalytic Activity, Application to Fe-Based Ammonia Synthesis

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#### Details of phonon calculations

In the phonon calculations, we first computed the force constants from the finite displacement approach implemented in phonopy.<sup>1</sup> Then the dynamical matrix was built from the derived force constants. Finally, the phonon frequencies were obtained at the specified K-points. The thermal properties, such as zero-point energy, entropy and free energy, were then computed from the statistical thermodynamics.<sup>2</sup> This makes it important to validate the convergence of K-points in phonon calculations. We used bulk Fe with  $2 \times 2 \times 2$  supercell to test the convergence of K-points. As shown in Table S1, the convergence of thermal properties from phonon calculations requires at least a  $2 \times 2 \times 2$  Kpoints. Therefore, we applied  $8 \times 8 \times 8$  Kpoints to obtain the phonon frequencies in all phonon and thermal properties calculations.

In the slab model, a  $1 \times 1 \times 1$  supercell was applied in the finite displacement calculations due to the large simulation systems. The phonon calculation and free energy correction were computed for the pure Fe slabs with N adsorbate, such as Fe-bcc(100), Fe-bcc(110) and Fe-bcc(211)R, at 673 K. Then the free energy correction is added to the electronic energy from DFT to obtain the system energy (slab + N adsorbate) at 673 K. Then, the same approach is used to obtain the free energy of bulk Fe (BCC) at 673 K. The free energy of N<sub>2</sub> gas molecule was obtained from previous study.<sup>3</sup> Finally the surface energy at 673 K is computed using the equation:

$$F_{\text{surface}} \equiv (F_{\text{slab}} - F_{\text{bulk}} - F_{\text{N}_2}) / (\text{Area}) \quad (\text{S1})$$

where  $F_{\text{slab}}$ ,  $F_{\text{bulk}}$  and  $F_{\text{N}_2}$  are free energies of slab, bulk Fe and gas phase N<sub>2</sub> by combining the electronic energy and free energy correction from phonon calculations. The computed surface energies by considering accurate phonon calculations are listed in Table 2 and compared to the estimation without phonon calculations. The comparison indicated that the surface energy ratios of various surfaces are only different by ~2% although the estimation values are higher than the calculation considering phonons. ~2% difference barely influence the Wulff construction using surface energy ratios and therefore, it is reliable to use the estimation values without the phonon calculations.

**Table S1.** Fe-bcc(100)→Fe-bcc(111) migration energies for bare surfaces,  $\Delta E_{\text{migr}}[\text{b}]$ , for the various dopants that satisfy  $\Delta E_{\text{migr}}[\text{b}] < 0$ . The (sub) represents the subsurface doping. Please note that the Ni prefers subsurface doping for Fe-bcc(111) while it prefers the top surface doping for Fe-bcc(100). Therefore, the most stable configurations are used to compute  $\Delta E_{\text{migr}}[\text{b}]$ .

<b>Elements</b>	<b><math>\Delta E_{\text{migr}}[\text{N}]</math> (eV)</b>
<b>Si (sub)</b>	-1.296
<b>Mo</b>	-0.575
<b>Tc</b>	-0.540
<b>Co (sub)</b>	-0.500
<b>Re</b>	-0.430
<b>Nb</b>	-0.428
<b>Cr</b>	-0.398
<b>W</b>	-0.394
<b>V</b>	-0.344
<b>Ni</b>	-0.256
<b>Y</b>	-0.241
<b>Ta</b>	-0.221
<b>Zr</b>	-0.197
<b>Ti</b>	-0.144
<b>Rh</b>	-0.134
<b>Os</b>	-0.117
<b>Tm</b>	-0.080
<b>Mn</b>	-0.077
<b>Sc</b>	-0.015
<b>Fe</b>	0

**Table S2.** Convergence test of Kpoints setup in the phonon calculations. The entropy (S) and enthalpy (H) was calculated at 673 K. The electronic energy is not included in the calculations.

<b>Fe-bulk (eV/atom)</b>	<b>Kpoints</b> $1 \times 1 \times 1$	<b>Kpoints</b> $2 \times 2 \times 2$	<b>Kpoints</b> $8 \times 8 \times 8$
ZPE	0.02955	0.04437	0.04411
Entropy (673 K)	0.00018	0.00044	0.00045
H - TS (673 K)	-0.0628	-0.1190	-0.1222

## References:

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