Supporting Information

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

Qi An[1*], Molly McDonald[1], Alessandro Fortunelli[2,3*], and William A. Goddard III[2*]

[1]Department of Chemical and Materials Engineering, University of Nevada-Reno, Reno, Nevada 89577, United States

[2]Materials and Process Simulation Center (MSC), California Institute of Technology, Pasadena, California 91125, United States

[3]CNR-ICCOM, Consiglio Nazionale delle Ricerche, ThC2-Lab, Pisa 56124, Italy

[*]Corresponding authors' E-mails: qia@unr.edu, alessandro.fortunelli@cnr.it, wag@caltech.edu

Details of phonon calculations

In the phonon calculations, we first computed the force constants from the finite displacement approach implemented in phonopy.[1] 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.[2] 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 absorbate) 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_2 gas molecule was obtained from previous study.[3] Finally the surface energy at 673 K is computed using the equation:

$$F_{surface} \equiv (F_{slab} - F_{bulk} - F_{N2}) / (Area) \qquad (S1)$$

where F_{slab}, F_{bulk} and F_{N2} are free energies of slab, bulk Fe and gas phase N_2 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, $\Delta E_{migr}[b]$, for the various dopants that satisfy $\Delta E_{migr}[b] < 0$. 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 $\Delta E_{migr}[b]$.

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

Fe-bulk (eV/atom)	**Kpoints** $1 \times 1 \times 1$	**Kpoints** $2 \times 2 \times 2$	**Kpoints** $8 \times 8 \times 8$
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:

(1) Togo, A.; Oba, F.; Tanaka, I. First-Principles Calculations of the Ferroelastic Transition between Rutile-Type and $CaCl_2$-Type SiO_2 at High Pressures. *Phys. Rev. B* **2008**, *78*, 134106.

(2) Dove, M. T. *Introduction to Lattice Dynamics*; Cambridge University Press: Cambridge (UK), 1993.

(3) Qian, J.; An, Q.; Fortunelli, A.; Nielsen, R. J.; Goddard III, W. A. Reaction Mechanism and Kinetics for Ammonia Synthesis on the Fe(111) Surface. *J. Am. Chem. Soc.* **2018**, *140*, 6288–6297.