Structure Reconstruction of Metal/Alloy in Reaction Conditions: A Volcano Curve?

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Content

The entropy of CO and NO_2 in the gas phase S_{gas} is calculated by[1]

$$S_{gas} = S(T, P^0) - R\ln\left(\frac{P}{P^0}\right)$$

where the P^0 is the standard atmospheric pressure (1 atm). T is the temperature, P is the pressure, and R is the gas constant. The $S(T, P^0)$ is the entropy of gas under the standard atmospheric pressure, fitted by the standard entropy data from the JANAF Tables.[2]

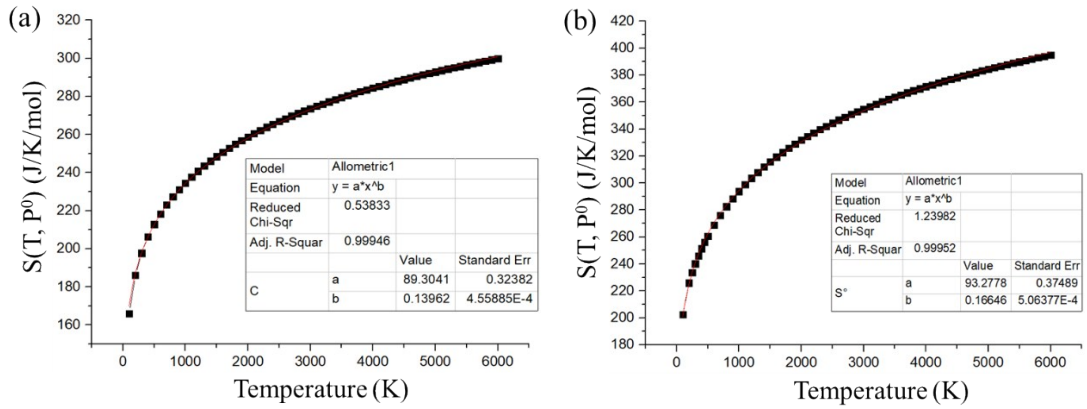

Figure S1. The fitted entropy of gas-phase (a) CO, (b) NO_2 under the atmospheric pressure. The standard entropy data refers to the JANAF Tables (http://kinetics.nist.gov/janaf/).

The slab model of calculating the adsorption energy of water molecules on the metal surfaces is shown in Fig. S2 (a) and (b).

$$E_{ads} = E_{surf+H_2O} - E_{surf} - E_{H_2O} \quad \text{(S1)}$$

The segregation energy of the solute atom under vacuum E_{seg} is calculated by the models in Fig. 2S (c) and (d).

$$E_{ads} = E_{surf}^{sol} - E_{bulk}^{sol} \quad \text{(S2)}$$

The adsorption energy of water molecule on the surface solute atom E_{ads}^{sol} is calculated by the models in Fig. 2S (d) and (e).

$$E_{ads}^{sol} = E_{surf+H_2O}^{sol} - E_{surf}^{sol} - E_{H_2O} \quad \text{(S3)}$$

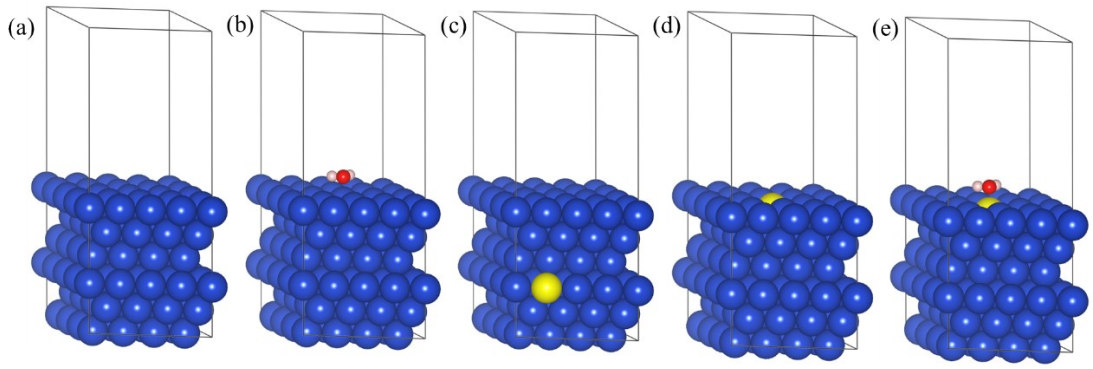

Figure S2. The (4 x 4) slab models of (a) Cu(111) clean surface, (b) the water molecule adsorbed

Cu(111) surface, (c) the solute atom located in the Cu(111) bulk, (d) the solute atom located on the Cu(111) surface, and (d) the water molecule adsorbed on the surface solute atom on the Cu(111) surface.

Table S1. The adsorption energies calculated using (4x4) slabs and (1x1) slabs and the lateral interaction w. All units are eV. The adsorption energies and lateral interaction energies of CO on the Cu surfaces are from our previous work [ref. S3].

	CO			**NO_2**		
	$E_{ads}(4x4)$	$E_{ads}(1x1)$	w	$E_{ads}(4x4)$	$E_{ads}(1x1)$	w
Cu(100)	-0.58	0.32	-0.22	-1.23	1.27	-0.63
Cu(110)	-0.64	-0.20	-0.22	-1.44	0.20	-0.82
Cu(111)	-0.47	0.73	-0.20	-0.90	1.90	-0.47

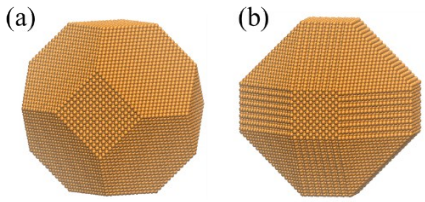

Figure S3. The structure of a 10 nm Cu nanoparticle under (a) vacuum and (b) 38 Pa water vapor at 220 ℃.

Reference

[S1] C. E. Wartnaby, A. Stuck, Y. Y. Yeo and D. A. King, Microcalorimetric Heats of Adsorption for CO, NO, and Oxygen on Pt{110}. *J. Phys. Chem.* 1996, **100,** 12483.

[S2] J. M.W. Chase, C.A. Davies, J.R. Downey, Jr. D.J. Frurip, R.A. McDonald, and A.N. Syverud, NIST-JANAF Thermochemical Tables, http://kinetics.nist.gov/janaf/, (accessed 09, 2016).

[S3] B. Zhu, J. Meng and Y. Gao, *J. Phy. Chem. C*, 2017, **121**, 5629.