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Supporting Information: Mechanism of Ammonia Synthesis on Fe_3Mo_3N

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***Ab initio* Thermodynamics Model**

To estimate the concentration of surface N vacancies on the $Fe_3Mo_3N(111)$ surface, the calculated DFT vacancy formation energies were combined with experimental gas phase thermochemical data using the general approach defined by Reuter et al.[1,2]

For N vacancy formation under hydrogenating conditions, the vacancy formation energy for *n* vacancies was defined as follows:

$$\Delta E_{Vac.} = E_{Fe_3Mo_3N\ n\ vac.} + nE_{NH_3(g)} - E_{Fe_3Mo_3N\ Pristine} - \frac{3n}{2}E_{H_2(g)} \qquad (1)$$

Where *E* refers to the DFT electronic energy for each species. Hence the Gibbs free energy of vacancy formation can be written as follows:

$$\Delta G_{Vac.} = g_{Fe_3Mo_3N\,n\,vac.} + n g_{NH_3(g)} - g_{Fe_3Mo_3N\,Pristine} - \frac{3n}{2} g_{H_2(g)} \qquad (2)$$

For a given component, the Gibbs free energy can be defined as the sum of the Helmholtz free energy and expansion work:

$$g = f + pV \qquad (3)$$

For the condensed phase components, the expansion work is negligible, hence:

$$g_{sol} \cong f \qquad (4)$$

Which can be decomposed into electronic, vibrational, and configurational contributions to the Helmholtz free energy:

$$g_{sol} \cong f_{elec} + f_{vib} + f_{conf} \qquad (5)$$

Ignoring the configurational term for the time being, it can be seen that for condensed phase components, f_{elec} is approximately equal to the DFT calculated electronic energy, and accounts for a greater contribution to g_{sol} than f_{vib}, given that atoms in the condensed phase are largely confined to lattice site. Moreover, since the expression for the Gibbs Free energy of vacancy formation involves subtracting Gibbs free energy terms for the pristine surface from the defective surface, it can be expected that there will be significant cancellation of the f_{vib} terms. Hence, it is reasonable to approximate the Gibbs free energy (excluding configurational contributions) for the condensed phase components to the DFT-calculated electronic energy:

$$g_{sol} \cong E_{sol} \qquad (6)$$

Turning now to the gas phase components, the molar Gibbs free energy, or chemical potential, at a given temperature and pressure is defined as follows:

$$\mu_{gas}(T, p) = \mu_{gas}(T, p^0) + k_B T Ln \frac{p}{p^0} \qquad (7)$$

Which can be considered in terms of individual components for enthalpy and entropy contributions to the chemical potential:

$$\mu_{gas}(T,p) = h_{gas}(T,p^0) - Ts_{gas}(T,p^0) + k_B T Ln\frac{p}{p^0} \qquad (8)$$

Which in turn can be re-written equivalently to include terms for the enthalpy contribution at 0K ($h_{gas}(0K,p^0)$), and for the DFT-calculated energy (E_{gas}):

$$\begin{aligned}\mu_{gas}(T,p) = &\left[h_{gas}(T,p^0) - h_{gas}(0K,p^0)\right] \\ &+ \left[h_{gas}(0K,p^0) - E_{gas}\right] \\ &+ E_{gas} - Ts_g(T,p^0) + k_B T Ln\frac{p}{p^0} \qquad (9)\end{aligned}$$

The expression on the first line of equation (9) corresponds to a correction for temperature dependence of gas phase entropy, which can be determined from experimental gas phase thermochemistry data publicly available online (e.g. via the NIST Webbook), and which we will define as Δh_{gas}:

$$h_{gas}(T,p^0) - h_{gas}(0K,p^0) = \Delta h_{gas} \qquad (10)$$

The expression on the second line of equation (9) can be interpreted as equivalent to contributions to the 0K enthalpy not accounted for by E_{gas}, i.e. contributions from zero-point vibrational energy, which can be approximated by taking the sum of the contributions from each gas phase vibrational frequency as determined by DFT:

$$h_{gas}(0K,p^0) - E_{gas} = E_{ZPE} \cong \sum_i^n \frac{h\upsilon_i}{2} \qquad (11)$$

Substituting equations (10) and (11) back into equation (9) gives the simplified expression, for which all terms can either be determined via DFT calculations, or from experimental gas phase thermochemistry data:

$$\mu_{gas}(T,p) = \Delta h_{gas} + E_{gas} + E_{ZPE} - Ts_{gas} + k_B T ln\frac{p}{p^0} \qquad (12)$$

Hence, combining equations (2), (6), and (7), we obtain the expression for the Gibbs free energy of vacancy formation entirely in terms that can be determined either via DFT or from gas phase thermochemistry data (as illustrated by equations (6) and (12)), plus the contribution from configurational entropy:

$$\Delta G_{vac} = E_{n.vac} - E_{pristine} + n\mu_{NH_3}(T,p) - \frac{3}{2}n\mu_{H_2}(T,p) - T\Delta s_{conf.} \quad (13)$$

The final term, the contribution to the Gibbs free energy from configurational entropy, has often proved challenging to approximate in practice. Reuter et. al proposed expressions for configurational entropy contributions that assume relatively low concentrations of defects in highly ordered lattices. However, in the present work, it is of interest to consider cases where potentially all of the surface lattice nitrogen is removed to compare with the Co_3Mo_3N, which is known experimentally to undergo mass loss of lattice N under certain conditions. Hence, it is not reasonable to use approximations for configurational entropy terms that inherently assume a very low surface vacancy concentration. Therefore, in the present model, we approach this by considering the range of vacancy concentrations spanned by the thin film model used. In the 2x2 thin film supercell, there are a total of 12 N atoms on each side of the slab model, giving a total of 24 surface N atoms that could potentially be removed from the surface. Given that the surface area of the slab is fixed in each case, the model can accommodate surface vacancy concentrations ranging from the pristine surface, to a single surface N-vacancy (i.e. removing 1/24 of the surface N atoms, for a vacancy concentration of 2.01 $\times 10^{21}$ cm^{-2}), and then in increments up to complete loss of surface lattice N, which corresponds to a vacancy concentration of 4.83 x 10^{22} cm^{-1}. Hence, for each surface vacancy concentration increment, the configurational entropy was approximated as follows: from the Boltzmann equation, the configurational entropy is defined thusly:

$$s = k_B LnW \quad (14)$$

Where W is the binomial coefficient:

$$W = \frac{N!}{n(N-n)!} \quad (15)$$

Hence, in the present work, configurational entropy is very coarsely approximated by taking the binomial coefficient for each vacancy concentration level, i.e. N = 24 and 0 < n < 24. Clearly, this approach is limited by the constraints imposed by the choice of surface cell size, but at least gives some appropriate weighting to high configurational entropy systems (i.e. intermediate vacancy concentrations). Even for the conditions giving the highest configurational entropy term (highest temperature within range, n = 12), the approximate configurational entropy contribution represents only ~8% of the vacancy formation energy excluding contributions from gas phase partial pressure and configurational entropy, hence the impact of using this limited approach is of negligible impact to the overall qualitative insights into vacancy concentration provided by the *ab initio* thermodynamics study.

To generate the contour plot (Figure 3), the Gibbs free energy of vacancy formation was determined for a range of sets of conditions according to equation (13); the $k_B T ln \frac{p}{p^0}$ contribution to the $\mu_{NH_3}(T, p)$ term was fixed at a partial pressure of 1 x 10^{-4} bar, assuming that the ammonia partial pressure remains low and constant relative to the H_2 partial pressure, since any NH_3 is assumed to be evolved via hydrogenation of surface lattice N. For each vacancy concentration increment, the vacancy formation energy component was determined as a multiple of the single vacancy concentration energy as reported in Table 1 in the main text; clearly, this approach neglects lateral interactions between vacancies, which are relatively small for low vacancy concentrations, as illustrated by the dual vacancy formation energy also presented in Table 1, although this would be expected to be much greater for higher vacancy concentrations. However, as Figure 3 qualitatively illustrates, such circumstances would only be expected to occur under the most extreme conditions, hence the thresholds for lower vacancy concentration levels can be considered to be more representative within the limitations of the model used. The contour plot shows the vacancy concentration which gives the most negative

Gibbs free energy of vacancy formation under a given set of conditions, and is therefore most thermodynamically favourable state within the confines of the model.

References

1 J. Rogal and K. Reuter, *Exp. Model. Simul. Gas-Surface Interact. React. Flows Hypersonic Flights*, 2007, 2-1-2–18.

2 K. Reuter, *Catal. Letters*, 2016, **146**, 541–563.