

Supplementary Materials

Phenol hydrogenation over H-MFI zeolite encapsulated platinum nanocluster catalyst

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Gibbs Free Energy for Gas Molecule

In order to incorporate the Gibbs free energy correction into a system, it is necessary to calculate the contributions of entropy and energy arising from translational, electronic, rotational, and vibrational motion. For example, the entropy (S) can be determined using the partition function¹

$$S = R \left(\ln (q_T q_e q_r q_v e) + T \left(\frac{\partial \ln q}{\partial T} \right)_V \right) \quad (\text{S1})$$

where q is the total partition function and equals $q_T q_e q_r q_v$. Here, e represents the gas constant (R) of 8.314 J/(mol·K), which is moved into the logarithm. q_T , q_e , q_r , q_v are the contributions of translational, electronic, rotational and vibrational motions, respectively, and T is temperature.

Similarly, the internal thermal energy (U) can be obtained from partition function:

$$U = RT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (\text{S2})$$

using the component partition functions of translational, electronic, rotational, vibrational contribution. The equations for these component partition functions can be

found at Ref. 1. Finally, the internal thermal energy and entropy correction can be calculated by:

$$U = U_t + U_e + U_v + U_r \quad (\text{S3})$$

$$S = S_t + S_e + S_v + S_r \quad (\text{S4})$$

Based on this, the Gibbs free energy can be derived:

$$G = E + \varepsilon_{ZPE} + \Delta U_{0 \rightarrow T} + PV + TS \quad (\text{S5})$$

where E is the electronic energy of the system, and the zero-point energy (ZPE) is given by the formula,

$$\varepsilon_{ZPE} = \frac{1}{2} \sum_i h\nu_i \quad (\text{S6})$$

ν represents the frequency of each vibrational mode. The variable i is freedom number of the molecule, with i equaling $3N-5$ for linear molecules and $3N-6$ for non-linear molecules. N is the number of atoms in the system. $\Delta U_{0 \rightarrow T}$ represents the internal energy difference between the temperatures of 0 and T K. P and V are the pressure and volume of the system, respectively.

Gibbs Free Energy for Adsorbed Molecule

For adsorbed molecules, the translation and rotation are constrained due to bonding with the substrate, leading to a reduction in their entropy contribution. Their contributions are often treated as a part of vibrational entropy. However, low vibrational frequencies can result in disproportionately large entropy contributions. To avoid this issue, frequencies below 50 cm^{-1} are typically set to 50 cm^{-1} . Consequently, the Gibbs free energy for adsorbed molecules can be expressed as:

$$G = E + \varepsilon_{ZPE} + \Delta U_{0 \rightarrow T} + TS \quad (\text{S7})$$

Unlike gas molecules, the Gibbs free energy for adsorbed molecules does not include the term PV . Additionally, the number of vibrational modes for adsorbed molecules is $3N$.

ab initio molecular dynamics simulation setup

In the ab initio molecular dynamics (AIMD) simulations, the Perdew-Burke-Ernzerhof exchange/correlation functionals² are used, along with norm-conserving Goedecker-Teter-Hutter pseudopotentials for the core electrons. A cutoff energy of 360 Ry is applied and dispersion forces are included using the DFT-D3 scheme³ in the calculations. The simulations are performed in the canonical NVT ensemble with a temperature of 500 K maintained using the Nose-Hoover thermostat.^{4,5} The equations of motion are integrated using the velocity Verlet method with a time step of 0.5 fs, and each system is equilibrated for 20 ps.

References

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