Supporting Information for

Liquid-Phase Effects on Adsorption Processes in Heterogeneous Catalysis

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Table S1. Lennard-Jones parameters of all elements in this study based on $V_{ij} = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6}$, where $\varepsilon$ is the depth of the potential well and $\sigma$ is the finite distance at which the inter-particle potential is zero. Ow and Hw represent oxygen and hydrogen of TIP3P/TIP4P-2005 water model, respectively. ‘Ho’ in the phenol molecule indicates the hydrogen of the OH functional group.

| Molecule or Metal | Element | $\varepsilon$ (kJ/mol) | $\sigma$ (Å) |
|-------------------|---------|------------------------|--------------|
| Pt                | 32.635  | 2.535                  |
| Cu                | 19.748  | 2.331                  |
| C                 | 0.495   | 3.911                  |
| O                 | 0.710   | 3.071                  |
| H                 | 0.126   | 1.978                  |
| Ethylene glycol   | Ow      | 0.636                  | 3.151        |
|                   | Hw      | 0.192                  | 0.400        |
| TIP3P water       | Ow      | 0.775                  | 3.159        |
|                   | Hw      | 0.192                  | 0.400        |
| TIP4P/2005 water  | Ow      | 0.775                  | 3.159        |
|                   | Hw      | 0.192                  | 0.400        |
| Carbon monoxide   | C       | 0.264                  | 3.491        |
|                   | O       | 0.651                  | 3.136        |
| Benzene           | C       | 0.293                  | 3.55         |
|                   | H       | 0.126                  | 2.420        |
|                   | C       | 0.293                  | 3.550        |
|                   | O       | 0.711                  | 3.070        |
| Phenol            | H       | 0.126                  | 2.420        |
|                   | Ho      | 0.126                  | 0.944        |

Advantages and limitations of the water-metal force field and overall potential energy function

The metal-water interaction is primarily represented by a Lennard-Jones (LJ) metal potential developed by Heinz et al. In the absence of adsorbate the electrostatic interaction between the metal atoms and the water molecules is practically non-existent (various charge models predict close to zero charges on the metal atoms). Heinz et al. employed experimentally determined densities and surface tensions of the low energy (111) facets of various fcc metals to obtain $\varepsilon$ and $\sigma$ parameters in the Lennard-Jones model. They then computed (using the fitted model) densities (cell parameters and the density of fcc metals), surface energies, interface energies, and mechanical properties and found a good agreement with experiments under ambient conditions with average deviations of 0.1, 3, 10, and 25%, respectively. The reasonable agreement for interfacial energies suggests that cavity formation energies are likely also reasonably accurate.
which is of high importance for this study. Nevertheless, this LJ potential is far from perfect. It favors water molecules to be located on hollow sites versus atop sites as measured experimentally. Also, the water oxygen shoulder peak at ~2 Å above the Cu(111) and Pt(111) surface predicted by AIMD simulations\textsuperscript{64} is not found with this force field. Thus, it is possible that that hydrogen bonding might not be described as reliably as desired and further improvements in the water-metal potential can certainly improve the predictability of our novel computational scheme for predicting aqueous phase effects on adsorption processes on metal surfaces. Still, we argue that the consequences of slightly favoring a wrong adsorption site are not necessarily as detrimental as one might believe given that at room temperature (and above) the interfacial water does not form an ice-like structure, but water molecules can be found at various positions. Also, we have previously compared the performance of the Lennard-Jones potential with the Spohr-Heinzinger potential\textsuperscript{45} that favors water molecule adsorption on atop position and the difference in activation and reaction free energies for O-H, C-H, and C-OH bond cleavages of adsorbed ethylene glycol over Pt(111) were found to be within 0.1 eV,\textsuperscript{44} suggesting that the consequences of the error of the Lennard-Jones potential not predicting the correct water molecule adsorption site is likely relatively small.

Next, our QM/MM potential energy considers polarization of the QM metal-adsorbate region by the MM water region which we find to be generally important and most critical for transition states with elongated bonds. Polarization also leads to some charge transfer between the metal atoms and the adsorbate, and a charge model is required to describe the changes in (classical) electrostatic interaction upon adsorption. The DDEC6 charge model is our preferred charge model (although we also used the NPA charge model in some select calculations in this study to numerically validate our implementation against previous calculations that utilized our old eSMS methodology that cannot describe adsorption (but only surface reaction) and that is somewhat slower) as it is believed to reproduce electrostatic properties, Pauling electronegativity trends, and chemical properties. Importantly, the resulting net atomic charges have also been shown to be meaningful inputs for simulations that use the CHARMM and AMBER force fields, i.e., well-validated force field parameters are available to simulate many systems with the DDEC6 charge model.\textsuperscript{39, 65-68} Nevertheless, the QM/MM potential energy function is certainly not perfect, and it is important to validate our QM/MM scheme against experimental data as done to some degree in this study by comparing our solvation effects on adsorption free energies against experimental data of phenol and benzene adsorption.
Adequately sampling of the potential energy surface for all relevant configurations of the system is a key for a reliable estimate of ensemble averages and a prediction of the liquid phase effect on free energies of elementary processes. Yet, extensive exploration of the configuration space for the relevant configurations is challenging due to the substantial number of solvent molecules in the system. In addition, it is not a priori obvious how much water sampling is required for adsorbed species on metal surfaces. Consequently, the average rotational correlation time for water molecules in proximity (up to 5 Å) of the adsorbates for each free energy calculation is computed. And the configuration space is then sampled long enough, relative to the average rotational correlation time, to assure that relevant configurations of the system are sampled sufficiently. A three-exponential fit to the rotational correlation time function of water molecules in 5 Å radius of each adsorbed species, investigated in this study, is presented in Figure S1. Table S2 also lists the average rotational correlation time and constants of the 3-exponential fits of Figure S1.

Table S2. Average rotational correlation time (RCT) and constants (in pico-second) of 3-Exponential fits

|              | EG on Cu(111) | EG on Pt(111) | CO on Cu(111) | CO on Pt(111) | Phenol on Cu(111) | Phenol on Pt(111) | Benzene on Pt(111) |
|--------------|---------------|---------------|---------------|---------------|-------------------|-------------------|-------------------|
| $a_1$        | 0.127         | 0.102         | 0.520         | 0.534         | 0.305             | 0.394             | 0.574             |
| $a_2$        | 0.447         | 0.451         | 0.354         | 0.360         | 0.512             | 0.436             | 0.312             |
| $\tau_1$    | 122.491       | 86.866        | 18.707        | 46.349        | 54.223            | 60.506            | 45.243            |
| $\tau_2$    | 2.176         | 2.416         | 2.330         | 2.143         | 4.106             | 4.102             | 6.542             |
| $\tau_3$    | 0.271         | 0.290         | 0.069         | 0.047         | 0.188             | 0.186             | 0.109             |
| RCT          | 115.0         | 76.6          | 17.4          | 45.0          | 48.5              | 56.5              | 42.4              |
Figure S1. Rotational correlation time function of liquid water molecules residing in a 5 Å radius of adsorbed ethylene glycol (C$_2$H$_6$O$_2^*$) species on Cu(111) and Pt(111) at 423 K, of adsorbed carbon monoxide (CO*) on Cu(111) and Pt(111) at 298 K, of adsorbed phenol (C$_6$H$_5$OH*) on Cu(111) and Pt(111) at 298 K, and of adsorbed benzene (C$_6$H$_6^*$) on Pt(111) at 298 K. The correlation time functions have been fitted using three exponential functions to obtain the average rotational correlation times (see Table S2).
QM/MM Free Energy Calculation

The explicit Solvation model for Metal Surfaces (eSMS) methodology\textsuperscript{12}, based on QM/MM-(M)FEP (free energy perturbation)\textsuperscript{13-14}, which has been implemented in our program packages and which was successfully employed in our previous studies for surface reactions,\textsuperscript{15-16} was used to carry out the free energy calculations. Computation of the free energy difference between two states was carried out using the Bennett Acceptance Ratio (BAR),\textsuperscript{17} which is a more efficient and precise way than exponential averaging (EXP) when two states are sampled\textsuperscript{18} since it uses both the forward and reverse distributions simultaneously. Finally, the whole free energy estimation procedure has been repeated three times, independently, by different initialization of the velocities using different seeds for the pseudorandom number generator\textsuperscript{19} implemented in the DL\_POLY program package, to establish 95\% confidence intervals for evaluating the adsorption free energy of the investigated adsorbates (assuming a normal distribution).\textsuperscript{20} More than three independent simulations were carried out only if these three experiments could not result in a 95\% confidence interval of lower than 0.05 eV. All uncertainties reported in this study are 95\% confidence intervals.

Implicit Solvation Calculations

Implicit solvation calculations were performed with the iSMS method,\textsuperscript{21} and VASPsol\textsuperscript{22-23} with a relative permittivity of water at desired reaction conditions.\textsuperscript{24} We used the default values for the VASPsol parameters. While these parameters are likely most accurate only for simulations at 298 K and not at 423 K, they are optimized parameters of the solvent model that cannot easily be obtained at other temperatures. All other computational details for periodic implicit solvation calculations were kept the same as in our periodic gas phase calculations.

Aqueous-phase phenol adsorption isotherm derivation

At equilibrium, the chemical potential for each species is equal in each phase. For phenol, chemical equilibrium is written as

\[
\hat{\mu}_\text{Ph}^G(T, P, y) = \hat{\mu}_\text{Ph}^L(T, P, x) = \hat{\mu}_\text{Ph}^a(T, \Phi, \theta),
\]  

(1)
where $\mu^G_{Ph}(T, P, y)$, $\mu^L_{Ph}(T, P, x)$, and $\mu^d_{Ph}(T, \Phi, \theta)$ are the mixture chemical potentials of phenol in the gas, aqueous, and two-dimensional adsorbed phase, respectively. $\Phi$ is a two-dimensional pressure on the lattice. The terms $y$, $x$, and $\theta$ are sets of the independent mol fractions in the gas and aqueous phases, and occupation fraction of the adsorbed phase respectively. The chemical equilibrium for hydrogen involves both phase and chemical reaction equilibrium due to the dissociation of the hydrogen molecule upon adsorption. Therefore, the chemical equilibrium for hydrogen is expressed as

$$\mu^G_{H_2}(T, P, y) = \mu^L_{H_2}(T, P, x) = 2\mu^d_{H}(T, \Phi, \theta). \quad (2)$$

To obtain the chemical potential of hydrogen and phenol in the adsorbed phase, we utilize a partition function proposed by Nitta et al.\textsuperscript{57,58},

$$lnQ^d = ln\left[\frac{M!}{(M-nN_{Ph}-N_H)!N_H!}\right] + ln\left[\frac{1}{N_{Ph}!M^{(n-1)}N_{Ph}}\right] + N_{Ph}\ln(j_{ad,Ph}) + \left\{\frac{N_{Ph}z_{Ph}kT}{kT} + \frac{N_Hz_HkT}{kT}\right\} - \frac{(nN_{Ph}z_{Ph})^2}{2MkT} - \frac{nN_{Ph}N_Hz_{Ph}z_H}{MkT} - \frac{(N_H)^2z_{Ph}z_H}{2MkT}, \quad (3)$$

where $M$ is the total number of lattice sites, $n$ is the number of lattice sites that phenol occupies upon adsorption, $j_{ad,Ph}$ and $z_{Ph}$ are parameters that only depend on temperature and describe the internal, vibrational, and flexibility degrees of freedom for phenol when it is adsorbed on the two-dimensional lattice, $\epsilon_i$ is the adsorption energy per molecule for adsorbate-surface interactions, and $\alpha_{l,j}$ is an interaction parameter for adsorbate-adsorbate interactions on the surface.

By taking the appropriate derivative of the partition function, we can obtain the chemical potentials in the adsorbed phase,

$$\frac{\mu^d_{Ph}}{kT} = ln(\theta_{Ph}) - nln(\theta_*) + n\theta_{Ph}\frac{\alpha_{Ph,Ph}kT}{kT} + n\theta_H\frac{\alpha_{Ph,H}kT}{kT} + \frac{\epsilon_{Ph}kT}{kT} - ln(j_{ad,Ph}z_{Ph}), \quad (4)$$

$$\frac{\mu^d_{H}}{kT} = ln(\theta_H) - ln(\theta_*) + \theta_H\frac{\alpha_{H,H}kT}{kT} + \theta_{Ph}\frac{\alpha_{Ph,H}kT}{kT} + \frac{\epsilon_HkT}{kT}, \quad (5)$$

where $\theta_{Ph} = N_{Ph}/M$ and $\theta_H = N_H/M$. $\theta_* = 1 - n\theta_{Ph} - \theta_H$ is the fraction of free sites.

To derive adsorption isotherm expressions, we utilize the conditions of chemical equilibrium discussed above. An ideal gas mixture condition for molecular hydrogen in the gas...
phase was used, and the ideal solution Henry’s law expression for the fugacity of phenol in the aqueous phase.

$$\frac{\mu_{H_2}}{kT} = \frac{\mu_{H_2}^{iq}(T,1\text{bar})}{kT} + \ln \left(\frac{P_{H_2}}{1\text{bar}}\right),$$  \hspace{1cm} (6)

$$\frac{\mu_{Ph}}{kT} = \frac{\mu_{Ph}^{iq}(T,1\text{bar})}{kT} + \ln \left(\frac{C_{Ph}K_{Ph}}{1\text{bar}}\right),$$  \hspace{1cm} (7)

where $P_{H_2}$ is the partial pressure of hydrogen in the gas phase, $C_{Ph}$ is the concentration of phenol in the aqueous phase in mol/liter, and $K_{H,Ph}$ is the Henry’s law constant for phenol in the aqueous phase with units of pressure divided by molarity.

By equating the chemical potentials, with the correct stoichiometry as necessary, we get the following expressions for the isotherms of phenol and hydrogen

$$\theta_{Ph} = (\theta_i) \exp \left[ -n \left( n \frac{\alpha_{Ph,Ph}}{kT} + \theta_H \frac{\alpha_{Ph,H}}{kT} \right) \right] K_{Ph}^{ad} C_{Ph} K_{H,Ph},$$  \hspace{1cm} (8)

$$\theta_H = \theta_i \sqrt{ \left\{ \exp \left[ -2 \left( n \frac{\alpha_{Ph,H}}{kT} + \theta_H \frac{\alpha_{H,H}}{kT} \right) \right] \right\} K_{H_2}^{ad} P_{H_2},}$$  \hspace{1cm} (9)

where the adsorption constants, $K_i^{ad}$, have units of inverse pressure and are equal to

$$K_{Ph}^{ad} = \frac{j_{ad,Ph} \xi_{Ph}}{1\text{bar}} \exp \left( \frac{-\varepsilon_{Ph}}{kT} \right) \exp \left( \frac{\mu_{Ph}^{iq}(T,1\text{bar})}{kT} \right),$$  \hspace{1cm} (10)

$$K_{H_2}^{ad} = \frac{1}{1\text{bar}} \exp \left( \frac{-2\varepsilon_H}{kT} \right) \exp \left( \frac{\mu_{H_2}^{iq}(T,1\text{bar})}{kT} \right).$$  \hspace{1cm} (11)

To get equations (8) and (9) into the form that we use in the main text, we need to make two more definitions. The first is related to the adsorbate-adsorbate interactions on the lattice, $\alpha_{i,j}$.

From inspection of equation (3), these adsorbate-adsorbate interactions are written on a site-site level of detail. To better match with our expressions in the main text, we will instead use molecule-molecule levels of detail. The alternative molecule-molecule parameters are expressed in terms of the site-site parameters as

$$\alpha_{Ph,Ph} = n^2 \alpha_{Ph,Ph}^{liq} ; \quad \alpha_{Ph,H}^{liq} = n \alpha_{Ph,H} ; \quad \alpha_{H,H}^{liq} = \alpha_{H,H}$$  \hspace{1cm} (12)
where the liq superscripts are used to signify that the interactions are influenced by the surrounding solvent.

The final update is to the adsorption energy term for phenol in equation (10). Let’s define two new terms as $\Delta G_{ph}^{gas} (\theta_{ph} = 0)$ and $\Delta \Delta G_{ph}^{gas-liq} (\theta_{ph} = 0)$. $\Delta G_{ph}^{gas} (\theta_{ph} = 0)$ is the change in Gibbs free energy of phenol adsorbing to our surface from the gas phase at low surface coverage of phenol. $\Delta \Delta G_{ph}^{gas-liq} (\theta_{ph} = 0)$ is the solvent effect on the Gibbs free energy of phenol adsorption in the limit of low phenol coverage. We can now write the adsorption energy for phenol as

$$\varepsilon_{ph} = \Delta G_{ph}^{gas} (\theta_{ph} = 0) + \Delta \Delta G_{ph}^{gas-liq} (\theta_{ph} = 0). \tag{13}$$

Plugging equation (13) into equation (10) yields

$$K_{ph}^{ad} = K_{eq,ph}^{gas} (\theta_{ph} = 0) \exp \left(-\frac{\Delta \Delta G_{ph}^{gas-liq} (\theta_{ph} = 0)}{kT} \right), \tag{14}$$

where

$$K_{eq,ph}^{gas} (\theta_{ph} = 0) = \frac{j_{ad,ph} \gamma_{ph}}{1 \text{bar}} \exp \left(-\frac{\Delta G_{ph}^{gas} (\theta_{ph} = 0)}{kT} \right) \exp \left(\frac{\mu_{ph}^{liq} (T, 1 \text{bar})}{kT} \right). \tag{15}$$

Plugging equation (12) and equation (14) into equations (8) and (9) yield

$$\theta_{ph} = K_{eq,ph}^{gas} (\theta_{ph} = 0) (\theta^*) n \left\{ \exp \left(-\left(\theta_{ph} \frac{\alpha_{ph,ph}^{liq}}{kT} + \theta_{H} \frac{\alpha_{H,ph}^{liq}}{kT} + \frac{\Delta \Delta G_{ph}^{gas-liq} (\theta_{ph} = 0)}{kT} \right) \right) \right\} C_{ph} K_{H,ph}, \tag{16}$$

$$\theta_{H} = \theta^* \left\{ \exp \left[-2 \left(\theta_{ph} \frac{\alpha_{ph,H}^{liq}}{kT} + \theta_{H} \frac{\alpha_{H,H}^{liq}}{kT} \right) \right] \right\} K_{H_2}^{ad} p_{H_2}. \tag{17}$$

We now assume that the partial pressure of hydrogen is sufficiently small to set the surface coverage of hydrogen to zero. This simplifies equation (16) to

$$\theta_{ph} = K_{eq,ph}^{gas} (\theta_{ph} = 0) (\theta^*) n \left\{ \right\} C_{ph} K_{H,ph}. \tag{18}$$
\[ \theta_{ph} = K_{eq,ph}^{gas}(\theta_{ph} = 0)(1 - n\theta_{ph})^n \exp \left\{ - \left( \theta_{ph} \frac{\gamma_{ph,ph}}{kT} + \frac{\Delta\Delta G_{ph}^{gas-liq}(\theta_{ph} = 0)}{kT} \right) \right\} C_{ph}K_{H,ph}. \]  

Equation (18) can be solved iteratively using fixed-point iteration that has unfortunately only a small convergence radius. Alternatively, we can use a one-dimensional root finder on Eq. 18.

\[ 0 = K_{eq,ph}^{gas}(\theta_{ph} = 0)K_{H,ph}C_{ph}(1 - n\theta_{ph})^n \exp \left\{ - \left( \Delta\Delta G_{ph}^{gas-liq}(\theta_{ph} = 0) + \gamma_{ph,ph,\theta_{ph}} \right) \right\} - \theta_{ph} \]  

We know a bracket for \( \theta_{ph} \) (between 0 and 1/n) such that any bracketing method such as bisection or better Brent’s method can be used to solve this equation for \( \theta_{ph} \). Note that the equations cannot be solved analytically for \( n \neq 1 \). Specifically, we solved Eq. (19) for \( n = 1 \) to 5. Once we have a function that can solve for \( \theta_{ph} \) for any given \( C_{ph} \), \( \Delta\Delta G_{ph}^{gas-liq}(\theta_{ph} = 0) \), and \( \gamma_{ph,ph,\theta_{ph}} \), we can optimize for \( \Delta\Delta G_{ph}^{gas-liq}(\theta_{ph} = 0) \) and \( \gamma_{ph,ph,\theta_{ph}} \).

Next, we can also test how the presence of \( \theta_{h} \) invalidates the results. Since Eq. 18 remains valid and \( \theta_{h} = \gamma_{H} \times \theta_{*} \) remains a good approximation at constant temperature and hydrogen partial pressure (\( \gamma_{H} \) thus includes both the unknown hydrogen pressure and equilibrium constant for hydrogen adsorption), we have \( 1 = \theta_{*} + \theta_{h} + n\theta_{ph} = \theta_{*}(1 + \gamma_{H}) + n\theta_{ph} \) or \( \theta_{*} = \frac{1 - n\theta_{ph}}{1 + \gamma_{H}} \) and we just have to solve Eq. 20 for possible values of the constant ‘\( \gamma_{H} \)’ of 0.1, 1, and 10:

\[ 0 = K_{ads,ph}^{gas}(\theta_{ph} = 0)K_{H,ph}C_{ph}\left( \frac{1-n\theta_{ph}}{1+\gamma_{H}} \right)^n \exp \left\{ - \left( \frac{\Delta\Delta G_{ph}^{gas-liq}(\theta_{ph} = 0) + \gamma_{ph,ph,\theta_{ph}}}{RT} \right) \right\} - \theta_{ph} \]
Table S3. Charges of the QM system (in e) in the initial state, where there exist electrostatic and van der Waals interactions between the solvent and the adsorbate, and in the final state, where all interactions have vanished as if the adsorbate was removed completely, for different adsorbates investigated in this work. The initial and final states correspond to states I and IV in Figure 1 in the main text, respectively. a) Reactant and transition states of O-H bond cleavage of EG on a Cu(111) surface model using the NPA charge model, b) CO on a Pt(111) surface model using the NPA and DDEC6 charge models, c) ethylene glycol (EG) on the Pt(111) and Cu(111) surfaces using the NPA charge model, d) CO on Pt(111) and Cu(111) surfaces using the DDEC6 charge model, e) phenol on the Pt(111) and Cu(111) surfaces using the DDEC6 charge model (Ho in the phenol molecule indicates the hydrogen of the OH functional group), and f) benzene on Pt(111) surface using DDEC6 charge model.

| Atom | Reactant State | Transition State | Initial | Final | Initial | Final |
|------|----------------|------------------|---------|-------|---------|-------|
|      | Initial | Final | Initial | Final | Initial | Final | Initial | Final |
| Cu   | 0.042   | 0.046 | 0.042   | 0.045 |         |       |
| Cu   | -0.020  | -0.021 | -0.025  | -0.019 |         |       |
| Cu   | 0.059   | 0.049 | 0.082   | 0.046 |         |       |
| Cu   | 0.017   | 0.015 | 0.011   | 0.011 |         |       |
| Cu   | -0.009  | -0.026 | -0.003  | -0.023 |         |       |
| Cu   | -0.011  | -0.025 | -0.007  | -0.019 |         |       |
| Cu   | 0.011   | 0.012 | 0.009   | 0.013 |         |       |
| Cu   | 0.027   | 0.031 | 0.047   | 0.029 |         |       |
| Cu   | 0.004   | 0.004 | 0.007   | 0.002 |         |       |
| Cu   | -0.056  | -0.081 | -0.030  | -0.082 |         |       |
| Cu   | -0.003  | 0.004 | 0.009   | -0.001 |         |       |
| Cu   | 0.026   | 0.030 | 0.010   | 0.034 |         |       |
| Cu   | -0.021  | -0.010 | -0.027  | -0.005 |         |       |
| Cu   | -0.024  | -0.022 | -0.003  | -0.024 |         |       |
| Cu   | -0.039  | -0.025 | -0.036  | -0.022 |         |       |
| Cu   | -0.004  | -0.005 | -0.004  | -0.011 |         |       |
| Cu   | -0.007  | -0.012 | -0.002  | -0.015 |         |       |
| Cu   | 0.029   | 0.035 | 0.045   | 0.037 |         |       |
| Cu   | -0.019  | -0.015 | -0.009  | -0.011 |         |       |
| Cu   | 0.063   | 0.065 | 0.057   | 0.064 |         |       |
| Cu   | 0.057   | 0.062 | 0.036   | 0.066 |         |       |
| Cu   | 0.018   | 0.011 | 0.014   | 0.007 |         |       |
| Cu   | 0.025   | 0.012 | 0.023   | 0.014 |         |       |
| Cu   | -0.009  | 0.005 | -0.012  | 0.001 |         |       |
| Cu   | 0.019   | 0.034 | 0.023   | 0.030 |         |       |
| Cu   | -0.051  | -0.027 | -0.034  | -0.025 |         |       |
| Cu   | -0.013  | -0.032 | -0.040  | -0.032 |         |       |
| Cu   | 0.038   | 0.030 | 0.038   | 0.030 |         |       |
| Cu   | 0.040   | 0.025 | 0.036   | 0.020 |         |       |
| Cu   | -0.058  | -0.030 | -0.067  | -0.026 |         |       |
| Cu   | 0.128   | 0.019 | 0.150   | 0.003 |         |       |
| Cu   | -0.043  | -0.028 | -0.061  | -0.032 |         |       |
| Cu   | 0.036   | 0.021 | 0.009   | 0.025 |         |       |
| Cu   | 0.003   | -0.002 | 0.000   | -0.003 |         |       |
| Cu   | -0.031  | -0.020 | -0.009  | -0.025 |         |       |
| Cu   | -0.074  | -0.034 | 0.197   | -0.011 |         |       |
| Cu   | -0.069  | -0.036 | 0.083   | -0.035 |         |       |
| Cu   | -0.029  | -0.018 | -0.017  | -0.019 |         |       |
| Cu   | 0.005   | -0.007 | -0.001  | 0.008 |         |       |
| Cu   | 0.014   | 0.015 | 0.014   | 0.015 |         |       |
| Atom | Cu Initial | Cu Final | Cu Initial | Cu Final |
|------|------------|----------|------------|----------|
| Cu   | -0.030     | -0.037   | 0.018      | -0.040   |
| Cu   | -0.023     | 0.019    | 0.107      | 0.023    |
| Cu   | -0.033     | -0.042   | 0.003      | -0.045   |
| Cu   | 0.007      | 0.021    | 0.009      | 0.018    |
| Cu   | 0.011      | 0.012    | 0.017      | 0.014    |
| Cu   | -0.041     | -0.047   | -0.034     | -0.050   |
| Cu   | -0.053     | -0.046   | -0.043     | -0.047   |
| Cu   | 0.019      | 0.014    | 0.025      | 0.013    |
| Cu   | 0.018      | 0.021    | 0.019      | 0.024    |
| Cu   | 0.024      | 0.024    | 0.013      | 0.020    |
| C    | -0.106     | 0.000    | -0.101     | 0.000    |
| C    | -0.097     | 0.000    | -0.096     | 0.000    |
| O    | -0.749     | 0.000    | -0.856     | 0.000    |
| O    | -0.790     | 0.000    | -0.780     | 0.000    |
| H    | 0.208      | 0.000    | 0.193      | 0.000    |
| H    | 0.216      | 0.000    | 0.199      | 0.000    |
| H    | 0.206      | 0.000    | 0.212      | 0.000    |
| H    | 0.173      | 0.000    | 0.212      | 0.000    |
| H    | 0.472      | 0.000    | -0.164     | 0.000    |
| H    | 0.483      | 0.000    | 0.479      | 0.000    |

| Atom | NPA Initial | NPA Final | DDEC6 Initial | DDEC6 Final |
|------|-------------|-----------|---------------|-------------|
| Pt   | 0.075       | 0.081     | 0.000         | -0.001      |
| Pt   | 0.076       | 0.080     | -0.003        | 0.000       |
| Pt   | 0.084       | 0.078     | 0.007         | 0.006       |
| Pt   | -0.093      | -0.082    | -0.001        | -0.003      |
| Pt   | 0.081       | 0.073     | 0.003         | 0.003       |
| Pt   | 0.089       | 0.087     | 0.008         | 0.000       |
| Pt   | -0.069      | -0.030    | -0.019        | 0.010       |
| Pt   | -0.010      | -0.018    | 0.010         | 0.006       |
| Pt   | 0.077       | 0.083     | -0.002        | -0.001      |
| Pt   | 0.096       | 0.094     | 0.003         | 0.001       |
| Pt   | -0.082      | -0.043    | -0.019        | 0.009       |
| Pt   | -0.054      | 0.002     | -0.011        | 0.016       |
| Pt   | -0.039      | -0.038    | 0.005         | 0.005       |
| Pt   | 0.086       | 0.097     | -0.001        | 0.000       |
| Pt   | 0.029       | 0.034     | -0.005        | -0.007      |
| Pt   | -0.029      | -0.040    | 0.010         | 0.006       |
| Pt   | -0.047      | -0.044    | 0.005         | 0.004       |
| Pt   | 0.035       | 0.029     | -0.010        | -0.010      |
| Pt   | 0.103       | 0.092     | 0.003         | 0.002       |
| Pt   | 0.056       | 0.061     | -0.008        | -0.006      |
| Pt   | 0.092       | 0.092     | 0.003         | 0.002       |
| Pt   | -0.064      | -0.049    | -0.020        | -0.018      |
| Pt   | 0.047       | 0.036     | -0.010        | -0.009      |
| Pt   | -0.054      | -0.051    | -0.011        | -0.013      |
| Pt   | 0.002       | 0.012     | -0.042        | -0.043      |
| Pt   | -0.021      | -0.029    | 0.042         | 0.043       |
| Pt   | -0.034      | -0.030    | 0.043         | 0.044       |
| Pt   | 0.003       | 0.009     | -0.041        | -0.043      |
| Pt   | -0.014      | -0.011    | -0.049        | -0.046      |
| Pt   | -0.051      | -0.034    | 0.017         | 0.040       |
| Pt   | -0.063      | -0.074    | -0.020        | -0.002      |
| Atom | EG on Pt(111) | EG on Cu(111) |
|------|---------------|---------------|
|      | Initial       | Final         | Initial       | Final         |
| Metal | 0.076         | 0.079         | 0.042         | 0.046         |
| Metal | 0.074         | 0.074         | -0.020        | -0.021        |
| Metal | 0.082         | 0.080         | 0.059         | 0.049         |
| Metal | -0.097        | -0.094        | 0.017         | 0.015         |
| Metal | 0.078         | 0.081         | -0.009        | -0.026        |
| Metal | 0.096         | 0.088         | -0.011        | -0.025        |
| Metal | -0.026        | -0.029        | 0.011         | 0.012         |
| Metal | -0.010        | -0.024        | 0.027         | 0.031         |
| Metal | 0.082         | 0.084         | 0.004         | 0.004         |
| Metal | 0.095         | 0.091         | -0.056        | -0.081        |
| Metal | -0.044        | -0.045        | -0.003        | 0.004         |
| Metal | 0.004         | 0.000         | 0.026         | 0.030         |
| Metal | -0.040        | -0.044        | -0.021        | -0.010        |
| Metal | 0.093         | 0.096         | -0.024        | -0.022        |
| Metal | 0.031         | 0.033         | -0.039        | -0.025        |
| Metal | -0.028        | -0.041        | -0.004        | -0.005        |
| Metal | -0.045        | -0.044        | -0.007        | -0.012        |
| Metal | 0.036         | 0.033         | 0.029         | 0.035         |
| Metal | 0.095         | 0.091         | -0.019        | -0.015        |
| Metal | 0.067         | 0.075         | 0.063         | 0.065         |
| Metal | 0.094         | 0.096         | 0.057         | 0.062         |
| Metal | -0.051        | -0.059        | 0.018         | 0.011         |
| Metal | 0.038         | 0.040         | 0.025         | 0.012         |
| Metal | -0.048        | -0.049        | -0.009        | 0.005         |
| Metal | 0.002         | 0.014         | 0.019         | 0.034         |
| Metal | -0.038        | -0.024        | -0.051        | -0.027        |
| Metal | -0.026        | -0.027        | -0.013        | -0.032        |
| Metal | -0.004        | 0.000         | 0.038         | 0.030         |
| Metal | -0.019        | -0.013        | 0.040         | 0.025         |
| Metal | -0.032        | -0.035        | -0.058        | -0.030        |
| Atom | CO on Pt(111) | CO on Cu(111) |
|------|---------------|---------------|
|      | Initial | Final | Initial | Final |
| Metal | -0.086 | -0.049 | 0.128 | 0.019 |
| Metal | -0.042 | -0.025 | -0.043 | -0.028 |
| Metal | -0.013 | -0.010 | 0.036 | 0.021 |
| Metal | -0.047 | -0.043 | 0.003 | -0.002 |
| Metal | -0.006 | -0.018 | -0.031 | -0.020 |
| Metal | 0.014 | -0.039 | -0.074 | -0.034 |
| Metal | -0.133 | -0.048 | -0.069 | -0.036 |
| Metal | -0.032 | -0.019 | -0.029 | -0.018 |
| Metal | -0.044 | -0.042 | 0.005 | -0.007 |
| Metal | 0.000 | -0.001 | 0.014 | 0.015 |
| Metal | -0.033 | -0.036 | -0.030 | -0.037 |
| Metal | -0.097 | -0.056 | -0.023 | 0.019 |
| Metal | -0.041 | -0.015 | -0.033 | -0.042 |
| Metal | -0.007 | -0.005 | 0.007 | 0.021 |
| Metal | 0.004 | 0.010 | 0.011 | 0.012 |
| Metal | -0.033 | -0.018 | -0.041 | -0.047 |
| Metal | -0.029 | -0.020 | -0.053 | -0.046 |
| Metal | -0.003 | -0.010 | 0.019 | 0.014 |
| Metal | -0.044 | -0.038 | 0.018 | 0.021 |
| Metal | 0.000 | 0.002 | 0.024 | 0.024 |
| Metal | -0.040 | -0.046 | 0.015 | 0.014 |
| C    | -0.107 | 0.000 | -0.106 | 0.000 |
| C    | -0.096 | 0.000 | -0.097 | 0.000 |
| O    | -0.748 | 0.000 | -0.749 | 0.000 |
| O    | -0.720 | 0.000 | -0.790 | 0.000 |
| H    | 0.215 | 0.000 | 0.208 | 0.000 |
| H    | 0.226 | 0.000 | 0.216 | 0.000 |
| H    | 0.219 | 0.000 | 0.206 | 0.000 |
| H    | 0.196 | 0.000 | 0.173 | 0.000 |
| H    | 0.486 | 0.000 | 0.472 | 0.000 |
| H    | 0.505 | 0.000 | 0.483 | 0.000 |
| Atom | Phenol on Pt(111) | Phenol on Cu(111) |
|------|------------------|------------------|
|      | Initial         | Final            | Initial         | Final            |
| Metal | -0.066          | -0.006           | 0.009           | 0.009            |
| Metal | 0.002           | -0.005           | 0.002           | -0.002           |
| Metal | -0.005          | -0.006           | 0.015           | 0.008            |
| Metal | -0.013          | -0.011           | -0.006          | -0.014           |
| Metal | 0.005           | 0.014            | -0.009          | 0.001            |
| Metal | 0.011           | 0.015            | 0.002           | 0.002            |
| Metal | -0.017          | -0.012           | 0.004           | -0.012           |
| Metal | -0.003          | -0.003           | -0.004          | -0.008           |
| Metal | -0.016          | 0.012            | 0.017           | 0.022            |
| Metal | -0.101          | 0.013            | -0.048          | -0.016           |
| Metal | -0.007          | 0.012            | 0.021           | 0.022            |
| Metal | -0.006          | -0.004           | -0.006          | -0.008           |
| Metal | 0.006           | -0.003           | -0.002          | 0.000            |
| Metal | -0.047          | 0.009            | -0.010          | 0.009            |
| Metal | -0.047          | 0.009            | -0.013          | 0.009            |
| Metal | 0.004           | -0.003           | -0.005          | 0.001            |
| Metal | 0.009           | 0.007            | 0.000           | -0.001           |
| Metal | -0.002          | 0.006            | -0.003          | 0.000            |
| Metal | 0.008           | 0.006            | -0.002          | -0.001           |
| Metal | -0.014          | -0.009           | 0.010           | 0.012            |
| Metal | -0.013          | -0.009           | 0.012           | 0.012            |
| Metal | -0.006          | -0.004           | 0.014           | 0.015            |
| Atom | Benzene on Pt(111) |
|------|-------------------|
|      | Initial | Final |
| Metal | -0.006  | -0.006 |
| Metal | 0.002   | -0.003 |
| Metal | -0.006  | -0.006 |
| Metal | -0.014  | -0.011 |
| Metal | 0.002   | 0.012  |
| Metal | 0.003   | 0.012  |
| Metal | -0.015  | -0.012 |
| Metal | -0.004  | -0.004 |
| Metal | -0.016  | 0.011  |
| Metal | -0.105  | 0.012  |
| Metal | -0.016  | 0.011  |
| Metal | -0.004  | -0.004 |

| Atom | Benzene on Pt(111) |
|------|-------------------|
|      | Initial | Final |
| Metal | -0.062  | -0.056 |
| Metal | -0.003  | -0.004 |
| Metal | -0.035  | -0.028 |
| Metal | 0.014   | 0.049  |
| Metal | -0.005  | 0.047  |
| Metal | -0.041  | -0.029 |
| Metal | -0.054  | -0.032 |
| Metal | 0.009   | 0.040  |
| Metal | 0.024   | -0.028 |
| Metal | -0.052  | 0.044  |
| Metal | -0.048  | -0.032 |
| Metal | -0.004  | -0.001 |
| Metal | 0.003   | 0.047  |
| Metal | 0.134   | -0.017 |
| Metal | 0.086   | -0.016 |
| Metal | 0.045   | 0.047  |
| Metal | -0.004  | 0.000  |
| Metal | -0.069  | -0.050 |
| Metal | 0.004   | 0.054  |
| Metal | 0.032   | -0.038 |
| Metal | 0.013   | 0.055  |
| Metal | -0.069  | -0.050 |
| Metal | -0.051  | -0.048 |
| Metal | 0.016   | 0.053  |
| Metal | 0.017   | 0.053  |
| Metal | -0.051  | -0.050 |
| Metal | -0.010  | -0.007 |
| Metal | -0.033  | -0.029 |
| Metal | -0.007  | -0.004 |
| C    | -0.201  | 0.000  |
| C    | -0.032  | 0.000  |
| C    | -0.053  | 0.000  |
| C    | -0.071  | 0.000  |
| C    | -0.134  | 0.000  |
| C    | 0.336   | 0.000  |
| O    | -0.406  | 0.000  |
| H    | 0.146   | 0.000  |
| H    | 0.127   | 0.000  |
| H    | 0.133   | 0.000  |
| H    | 0.145   | 0.000  |
| Ho   | 0.341   | 0.000  |
| Element | Value 1  | Value 2 |
|---------|---------|---------|
| Metal   | 0.005   | -0.003  |
| Metal   | -0.046  | 0.010   |
| Metal   | -0.045  | 0.011   |
| Metal   | 0.006   | -0.002  |
| Metal   | 0.007   | 0.006   |
| Metal   | -0.003  | 0.005   |
| Metal   | 0.006   | 0.005   |
| Metal   | -0.012  | -0.008  |
| Metal   | -0.011  | -0.007  |
| Metal   | -0.005  | -0.003  |
| Metal   | -0.061  | -0.055  |
| Metal   | -0.005  | -0.003  |
| Metal   | -0.037  | -0.030  |
| Metal   | 0.010   | 0.048   |
| Metal   | 0.011   | 0.049   |
| Metal   | -0.037  | -0.030  |
| Metal   | -0.053  | -0.031  |
| Metal   | 0.011   | 0.043   |
| Metal   | 0.031   | -0.027  |
| Metal   | 0.010   | 0.042   |
| Metal   | -0.053  | -0.031  |
| Metal   | -0.005  | 0.000   |
| Metal   | 0.006   | 0.047   |
| Metal   | 0.129   | -0.016  |
| Metal   | 0.130   | -0.016  |
| Metal   | 0.006   | 0.047   |
| Metal   | -0.004  | 0.000   |
| Metal   | -0.068  | -0.049  |
| Metal   | 0.006   | 0.055   |
| Metal   | 0.025   | -0.039  |
| Metal   | 0.004   | 0.053   |
| Metal   | -0.069  | -0.050  |
| Metal   | -0.053  | -0.050  |
| Metal   | 0.018   | 0.054   |
| Metal   | 0.019   | 0.054   |
| Metal   | -0.052  | -0.049  |
| Metal   | -0.010  | -0.007  |
| Metal   | -0.033  | -0.028  |
| Metal   | -0.011  | -0.008  |
| C       | -0.087  | 0.000   |
| C       | -0.042  | 0.000   |
| C       | -0.045  | 0.000   |
| C       | -0.089  | 0.000   |
| C       | -0.046  | 0.000   |
| C       | -0.042  | 0.000   |
| H       | 0.133   | 0.000   |
| H       | 0.123   | 0.000   |
| H       | 0.124   | 0.000   |
| H       | 0.134   | 0.000   |
| H       | 0.124   | 0.000   |
| H       | 0.124   | 0.000   |
Table S4. Values for the parameter $\delta$ in $V_{ij} = (1 - \lambda) \left[ \frac{A}{(r_{ij}^2 + \delta \lambda)^{6}} - \frac{B}{(r_{ij}^2 + \delta \lambda)^{3}} \right]$ for interactions used in this study. As recommended by Zacharias et al.\textsuperscript{25}, the parameter $\delta$ was chosen as the square of the vdW radius of the interacting atoms to allow for a smooth transition between an atom present on the surface and filling the cavity after the molecule is annihilated. Ow and Hw represent the oxygen and hydrogen of the TIP3P (TIP4P/2005 water model for the benzene calculations) water model, respectively. Ho in the phenol molecule indicates the hydrogen of the OH functional group.

| Adsorbate   | Interacting term | $\delta(\text{Å}^2)$ |
|-------------|------------------|---------------------|
| Ethylene glycol | C-Ow            | 12.468              |
|              | O-Ow            | 9.678               |
|              | H-Ow            | 6.574               |
|              | H-Hw            | 1.414               |
| Carbon monoxide | C-Ow          | 12.184              |
|              | O-Ow            | 9.831               |
|              | C-Ow            | 11.223              |
|              | O-Ow            | 9.672               |
| Phenol      | H-Ow            | 7.756               |
|              | Ho-Ow           | 4.190               |
|              | H-Hw            | 1.988               |
|              | Ho-Hw           | 0.452               |
| Benzene     | C-Ow            | 11.253              |
|              | C-Hw            | 3.901               |
|              | H-Ow            | 7.781               |
|              | H-Hw            | 1.988               |
Figure S2. Scaling of the Lennard-Jones potential interaction between the oxygen of the CO molecule and the oxygen of the TIP3P water model, O-Ow. $\lambda = 0$ indicates the regular LJ potential, increasing $\lambda$ gradually decreases the interaction, and finally, $\lambda = 1$ leads to a complete removal of the LJ potential as if there were no adsorbate on the surface.

Table S5. Contributions to the aqueous-phase effect on the free energy of the low coverage desorption ($\Delta \Delta G^\text{liq-gas}_{\text{Adsorbate}} = -\Delta \Delta G^\text{gas-liq}_{\text{Adsorbate}}$) of the reactant and transition states of the O-H bond cleavage of ethylene glycol over a Cu(111) surface at 423 K (see Figure 2a in the main text). $\Delta \Delta G^\text{gas-liq}_{\text{Adsorbate}}$ also shows the overall aqueous-phase effect on the free energy of the low coverage adsorption of the states computed with QM/MM-FEP scheme proposed in this study, as well as two well-known implicit solvation schemes: iSMS and VASPsol. For the QM/MM-FEP calculations, the 95% confidence interval (based on limited water sampling) is given, assuming a normal distribution. All numbers are in eV.

| Adsorbate | Contributions to $\Delta \Delta G^\text{liq-gas}_{\text{Adsorbate}}$ in QM/MM-FEP scheme | $\Delta \Delta G^\text{gas-liq}_{\text{Adsorbate}}$ |
|-----------|------------------------------------------------------------------------------------------|-----------------------------------------------|
|          | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) | $I_{\text{opt}}$-I (To OPT adsorbate in Liquid) |
| Reactant state | 0.04 | 0.07 ± 0.00 | 0.49 ± 0.00 | -0.05 ± 0.01 | -0.64 ± 0.00 | -0.05 ± 0.00 | 0.14 ± 0.01 | 0.02 | -0.15 |
| Transition state | 0.11 | 0.02 ± 0.00 | 1.25 ± 0.00 | -0.21 ± 0.03 | -0.56 ± 0.01 | -0.11 ± 0.00 | -0.48 ± 0.03 | 0.00 | -0.21 |
Table S6. Number of hydrogen bonds (H-bond) between adsorbate and water molecules (we employed a geometric definition in which a hydrogen bond exists if the distance between the donor oxygen (O_d) and the acceptor oxygen (O_a), ROO, is less than 3.2 Å and the angle $\angle$HO_dO_a is smaller than 20°; see Figure S13) and number of sites occupied by adsorbate (#Site). These two descriptors were then used in a linear model, $\frac{y - \bar{y}}{s_y} = \alpha_1 \frac{f_1 - \bar{f}_1}{s_{f_1}} + \alpha_2 \frac{f_2 - \bar{f}_2}{s_{f_2}}$ ($s$ is the standard deviation and bar sign shows mean), as $f_1$ and $f_2$ respectively, for estimating aqueous-phase effects on the free energies of adsorption ($\Delta\Delta G_{gas-liq}^{Adorbate} = \Delta G_{g=1}^{Adorbate} - \Delta G_{gas}^{Adorbate}$), computed by the proposed scheme in this work (QM/MM-FEP). $\alpha_1$ and $\alpha_2$ are -0.44 and 0.86, respectively, which indicates a somewhat larger importance of the size of the adsorbate (cavity formation) than the H-bond.

| Adsorbate / Surface / T(K) | H-bond | #Site | $\frac{\Delta\Delta G_{gas-liq}^{Adorbate} - \Delta G_{gas}^{Adorbate}}{s_{\Delta\Delta G_{gas-liq}^{Adorbate}}}$ | QM/MM-FEP | Fit | |Error|
|---------------------------|--------|------|-------------------------------------------------|------------|----|--------|
| CO / Cu(111) / 298        | 0.12   | 1    | -0.82                                           | -0.68      | 0.14 |
| CO / Pt(111) / 298        | 0.08   | 1    | -0.61                                           | -0.65      | 0.04 |
| Phenol / Cu(111) / 298    | 0.44   | 5    | 1.13                                            | 1.08       | 0.05 |
| Phenol / Pt(111) / 298    | 0.41   | 5    | 0.88                                            | 1.10       | 0.22 |
| Benzene / Pt(111) / 298   | 0.00   | 4    | 1.02                                            | 0.90       | 0.12 |

Figure S3. Parity plot of the solvent effects on the adsorption of different adsorbates at 298 K. The plot compares the aqueous-phase effect on adsorption free energy computed by eSMS (QM/MM-FEP in Table 1 in the main text) against the model-predicted aqueous-phase effect. See Table S6 for more information about the model we used for these correlations.
Table S7. Number of displaced water molecules by adsorbate (#Water Displaced) for CO, phenol, and benzene adsorption over Pt(111) facet at 298 K. #Water Displaced is calculated as the difference between the number of water molecules within the first peak of the height distribution function (up to 4Å height from the surface metal; see Figure S4) for the adsorbate and for free surface without adsorbate system. This is repeated for 3 independent simulations performed and 95% confidence interval is reported.

| Adsorbate | #Water Displaced |
|-----------|-----------------|
| CO        | 1.88 ± 0.71     |
| Phenol    | 5.46 ± 0.97     |
| Benzene   | 4.43 ± 0.49     |
Figure S4. Height distribution function of water O for adsorption of different adsorbates studied in this work over the (111) facet of Cu and Pt surfaces. Y axis indicates the number of water molecules from the surface metal plane.
Figure S5. Average (of three independent simulations) free energy profile of the desorption of a CO molecule from a Pt(111) surface model at 298 K using the natural population analysis (NPA) charge model. $\Delta \Delta G (\Delta \Delta G_{CO}^{liq\rightarrow gas})$ is the aqueous-phase effect on the low coverage desorption free energy of CO.
Figure S6. Average (of three independent simulations) free energy profile for the desorption of a benzene (C₆H₆) molecule from a Pt(111) surface model at 298 K in the presence of an aqueous phase. ΔΔ\(G\) (ΔΔ\(G\)\text{\(\text{Benzene}\))\text{\(\text{liq}\)->\text{gas}\)) is the aqueous-phase effect on the low coverage desorption free energy of benzene.
Figure S7. Gas-phase optimized geometries of adsorbed species studied in this work: a) ethylene glycol (EG) over a Cu(111) surface model, b) transition state of O-H bond cleavage of EG over the Cu(111) surface model, c) EG over a Pt(111) surface model, d) CO over the Cu(111) surface model, e) CO over the Pt(111) surface model, f) phenol over the Cu(111) surface model, g) phenol over the Pt(111) surface model, and h) benzene over the Pt(111) surface model.
Figure S8. Fits of equation 7 in the main text (adsorption isotherm) to the experimental data (green circles) of aqueous-phase adsorption of phenol at 298 K on a Pt(111) catalyst surface from Singh et al.\textsuperscript{27-28} for two different regions: low and high phenol concentrations. The $\gamma_H$ parameter represents the hydrogen surface coverage relative to the free site coverage ($\gamma_H = 0$ shows zero H coverage approximation and $\gamma_H = 10$ means the H coverage is 10 times as large as the free site coverage), $n$ represents the number of sites a phenol molecule occupies when adsorbed on the surface, $\alpha$ ($\alpha_{\text{Ph,Ph}}^{\text{liq}}$) is a constant associated to phenol-phenol lateral interactions on the surface in water, and $\Delta\Delta G$ ($\Delta\Delta G_{\text{Ph,Ph}}^{\text{gas-liq}}(\theta_{\text{Ph}} = 0)$) is the solvent effect on the aqueous-phase low coverage phenol adsorption on the surface. SSR is the sum of squared residuals, which shows the error associated with each fit. Fits with higher $n$ predict the lower concentration region better, while fits with smaller $n$ predict the higher concentration region better. However, the fits suggest that $\Delta\Delta G_{\text{Ph}}^{\text{gas-liq}}(\theta_{\text{Ph}} = 0)$ is quite independent of these two fit regions.

Figure S9. Adsorbed phenol orientations at different coverages in the gas phase. At low coverage, phenols adsorb horizontally parallel to the surface, while at high coverage, they adsorb slanted to occupy less space on the surface.
Figure S10. Fits of equation 7 in the main text (adsorption isotherm) to the experimental data (green circles) of aqueous-phase phenol adsorption on a Pt(111) catalyst surface at 283 K from Singh et al. The parameter $\gamma_H$ represents the hydrogen surface coverage relative to the free site coverage ($\gamma_H = 0$ shows zero $H$ coverage approximation and $\gamma_H = 10$ means the $H$ coverage is 10 times as large as the free site coverage), $n$ represents the number of sites a phenol molecule occupies when adsorbed on the surface, $\alpha$ ($\alpha_{Ph,Ph}$) is a constant associated to phenol/phenol lateral interactions on the surface in water, and $\Delta\Delta G (\Delta\Delta G_{Ph}^{gas-liq}(\theta_{Ph} = 0))$ is the aqueous-phase effect on the low coverage phenol adsorption free energy on the surface. SSR is the sum of squared residuals, which shows the error associated with each fit.
Figure S11: Fits of equation 7 in the main text (adsorption isotherm) to the experimental data (green circles) of aqueous-phase phenol adsorption on a Pt(111) catalyst surface at 288 K from Singh et al. See the caption of Figure S10 for detailed explanations.
**Figure S12.** Fits of equation 7 in the main text (adsorption isotherm) to the experimental data (green circles) of aqueous-phase phenol adsorption on a Pt(111) catalyst surface at 314 K from Singh et al. See the caption of Figure S10 for detailed explanations.
**Figure S13.** Graphical representation of a geometric hydrogen bond definition used in this study. In the picture shown, water is the donor of hydrogen bonding, and ethylene glycol is the acceptor of hydrogen bonding.
| Acronym or Method         | Description                                                                                                                                                                                                 |
|--------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| AIMD method               | *Ab initio* molecular dynamics simulations in which molecular dynamics (MD) simulations are performed on a potential energy surface that is computed “on the fly” by electronic structure calculations.                   |
| BAR method                | Bennet Acceptance Ratio method used to compute the free energy difference in an FEP step by using ensemble data from both states which makes it significantly more accurate than exponential averaging that only uses the ensemble from one state. |
| COSMO-RS                  | An implicit solvation scheme designed for molecules and systems with non-periodic boundary conditions.                                                                                                    |
| DDEC6 charge model        | A refinement of the Density Derived Electrostatic and Chemical (DDEC) approach charge model. It was used in this study to obtain the charges of the QM system needed for the MM simulations. The DDEC6 charges are somewhat smaller than the NPA charges and they are likely a better match for the Lennard Jones potential parameters of the force field than the NPA charges. |
| eSMS method               | Explicit solvation scheme for metal surfaces and other interface systems that is based on a QM/MM description of a (periodic) reaction system and free energy perturbation of the MM atom coordinates to compute free energy differences of systems at solid-liquid interfaces. It assumes that the harmonic approximation or simple corrections to the harmonic approximation are valid for the QM atom coordinates and that the MM atom coordinates can be separated from the QM atom coordinates during the free energy calculation. This method is further developed in this paper. |
| Explicit solvation model  | A solvation model in which the solvent molecules are explicitly included as distinct molecules in the simulation system.                                                                                       |
| FEP step                  | A single free energy perturbation step in which the system is perturbed and the free energy change between the original and...
perturbed system is computed. Due to limitations in configuration space sampling and to reduce the error in the free energy calculation, the FEP step is typically made small enough, < 2kB T, to ensure significant configuration space overlap between the two states. In principle, the FEP procedure is also valid for large changes in free energy between states, but the calculation error might increase due to limited sampling.

| Term                  | Description                                                                 |
|-----------------------|-----------------------------------------------------------------------------|
| Implicit solvation model | A solvation model that describes the solvent as an isotropic continuum instead of a collection of solvent molecules. To still describe the solvent-solute interaction, these continuum solvation models (CSM) possess model parameters such as the dielectric constant and surface tension terms that need to be parameterized against experimental data. |
| iSMS method           | An implicit solvation scheme based on COSMO-RS that is designed for solid-liquid interfaces such as liquid water-metal surface interfaces that require periodic boundary conditions for the surface model. |
| MM system/subsystem   | The region which is treated at the MM level of theory. For example, in a metal-catalyzed adsorption reaction, the bulk of the solvent molecules and the nonreactive part of the simulation system. |
| NPA charge model      | Natural population analysis (NPA) charge model that is based on the Natural bond order (NBO) localization of molecular orbitals into bond orbitals method. This charge model is less basis set dependent than Mulliken population analysis and is implemented in the TURBOMOLE program package. It was used in this study to obtain the charges of the QM system needed for the MM simulations. |
| PEECM method          | Periodic electrostatic embedded cluster method implemented in the TURBOMOLE program package. It was used in this study to |
describe the effect of the TIP3P (TIP4P/2005) water point charges on the quantum chemically described cluster model.

| QM system/subsystem | The region of interest which is treated quantum mechanically. For example, in a metal-catalyzed adsorption reaction, adsorbate, active site and its immediate metal neighbors are treated from first principles, i.e., DFT. |
|---------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| QM/MM system        | The simulation system including QM and MM subsystems.                                                                                                                                               |
| QM/MM method/scheme/approach | An approach that describes the region of interest Quantum Mechanically (QM or DFT) and the remainder of the system Molecular Mechanically (MM) using, e.g., classical force fields |
| QM/MM-FEP method/scheme/approach | A class of QM/MM methods in which free energy perturbation theory (FEP) is used on a QM/MM potential energy surface to compute the free energy change along a process coordinate |
| VASP sol method     | An implicit solvation scheme implemented in the VASP program package for systems with periodic boundary conditions.                                                                                |
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