

Polyoxometalate Grafting onto Silica: Stability Diagrams of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ on $\{001\}$, $\{101\}$, and $\{111\}$ β -Cristobalite Surfaces Analyzed by DFT - Supporting Information

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To evaluate the Gibbs free energy of dehydroxylation, we make some approximations and assumptions to avoid unnecessary computational effort in our model, namely, i) the translation and rotation partition function contributions of the surface and bulk to the Gibbs free energy are neglected (bulk and surfaces are considered to be immobile), ii) the frequencies of vibration of the system remain unchanged in the reaction, which permits to neglect the contributions of the partition function of vibration and of the zero point energy (ZPE) to the Gibbs free energy. Then, for a dehydroxylation reaction that releases one water molecule in the gas phase, the Gibbs free energy is given by the equation:

$$\Delta_r G = \Delta_r E - RT \left(\ln \left(q_{\text{r}_{\text{H}_2\text{O}}} q_{\text{t}_{\text{H}_2\text{O}}} \right) - \ln \left(\frac{P_{\text{H}_2\text{O}}}{P^\circ} \right) \right) \quad (1),$$

where $\Delta_r E$ is the reaction (electronic) energy, $q_{\text{r}_{\text{H}_2\text{O}}}$ and $q_{\text{t}_{\text{H}_2\text{O}}}$ the rotation and translation partition functions of gas phase water, respectively, and $P_{\text{H}_2\text{O}}$ the water partial pressure.

Similar approximations have been used before in a study of alumina²⁸ and silica dehydroxylation.^{PCCP2010} Further information about the error committed when doing such approximations are given in ref. PCCP2010.

Concerning the Gibbs free energies of the grafting of the polyoxometalate onto the silica surfaces, the same assumptions than above are made: the translation and rotation partition functions of physisorbed ($\text{POM}\bullet\text{S}$), tri-covalently bonded ($\text{POM}\equiv\text{S}$), bi-covalently bonded ($\text{POM}=\text{S}$), and mono-covalently bonded ($\text{POM}-\text{S}$) polyoxometalate onto silica surfaces are neglected (the support is considered immobile), and the frequencies of vibration are considered unchanged in the covalent and hydrogen-bonded chemisorbed states, which allows us to neglect the contribution of the zero point energies of vibration (ZPE) and of the partition functions of vibration (q_v). Then, for instance, the following equation is used to obtain the Gibbs free energy in the reaction $\text{POM}\bullet\text{S}\rightarrow\text{POM}\equiv\text{S}+3\cdot\text{H}_2\text{O}_{(\text{g})}$:

$$\Delta_r G_{\text{c-p}} = E_{\text{POM}\equiv\text{S}} + 3E_{\text{H}_2\text{O}} - E_{\text{POM}\bullet\text{S}} - 3RT \left(\ln \left(q_{r_{\text{H}_2\text{O}}} q_{t_{\text{H}_2\text{O}}} \right) - \ln \left(\frac{P_{\text{H}_2\text{O}}}{P^\circ} \right) \right) \quad (2),$$

where $E_{\text{POM}\equiv\text{S}}$, $E_{\text{POM}\bullet\text{S}}$, and $E_{\text{H}_2\text{O}}$ are the electronic energies of the 3-covalently bonded POM, the physisorbed POM onto the surface, and H_2O , respectively, $q_{r_{\text{H}_2\text{O}}}$ and $q_{t_{\text{H}_2\text{O}}}$ are the partition functions of rotation and translation of H_2O , respectively, and $P_{\text{H}_2\text{O}}$ the partial pressure of $\text{H}_2\text{O}_{(\text{g})}$. Equivalent equations are obtained for di- and mono-covalently bonded POM onto the silica surfaces.