Supporting Information

Polyoxometalates adsorbed on Metallic Surfaces: Immediate reduction of $SiW_{12}O_{40}^{4-}$ on Ag(100)

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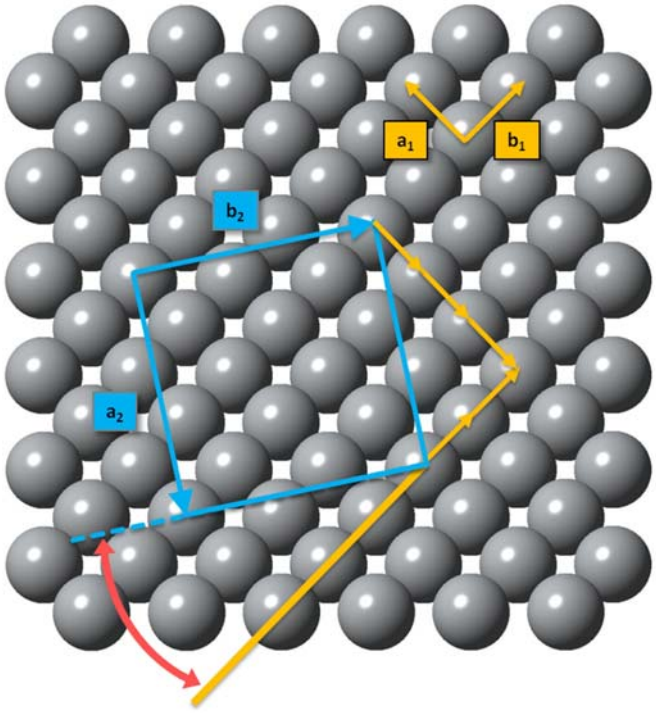
Figure S1. Representation of the adsorbate unit cell proposed by Gewirth and coworkers. The length of the surface unit cell vectors $\mathbf{a_1}$ and $\mathbf{b_1}$ is related to the bulk unit cell parameter, a_{bulk}. The Ag bulk parameter has been optimized at 4.15876 Å.[1] The length of the adsorbate unit cell vectors $\mathbf{a_2}$ and $\mathbf{b_2}$ is 10.6028 Å, which is obtained by means of a_1 unit cell vectors, as shown in the figure. The angle between vectors $\mathbf{a_2}$ and $\mathbf{b_2}$ is 90.0º (square unit cell). The angle between vectors $\mathbf{a_2}$ and $\mathbf{a_1}$ is 33.69º. Using Wood notation, the adsorbate unit cell is labeled as $\sqrt{13}x\sqrt{13}\,R33.69^o$.



$$|\overrightarrow{a_1}| = |\overrightarrow{b_1}| = \frac{\sqrt{2}}{2} \cdot a_{bulk}$$

$$|\overrightarrow{a_2}| = |\overrightarrow{b_2}| = \sqrt{13} \cdot a_1$$

$$\widehat{a_1 a_2} = 33.69^o$$

Figure S2. Top side of the polyhedral representation for the 2x2 unit cell with respects to the $\sqrt{13}x\sqrt{13}\,R33.69^{o}$. This representation is previous to incorporate water molecules and counterions.

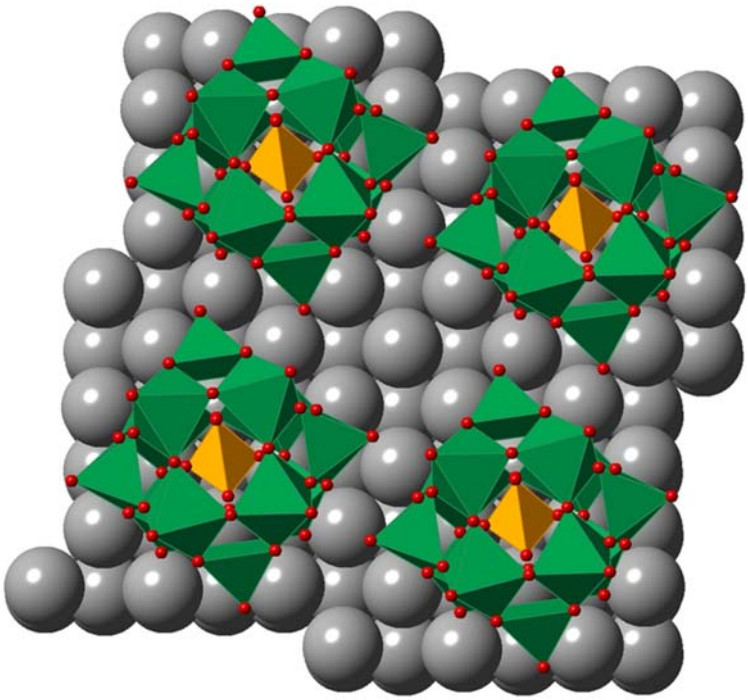


Figure S3. Polyhedral and balls and stick representation for a snapshot taken from the trajectory we obtained by means of MD simulation. a) Representation for the complete system and b) Selected portion (cut-off at 20 Å) used to compute the electronic structure.

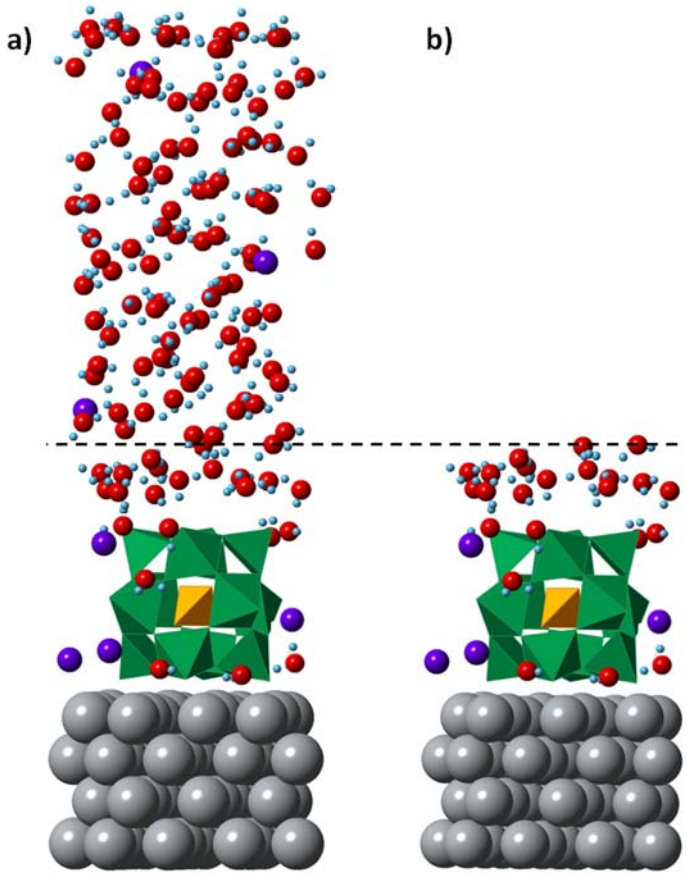


Figure S4. Projected density of states for silver in H_{37} (red line) and H_{37} with embedding effects (blue line). The reader should notice that the position of the Ag band suffers no change when the water and the counterions are considered.

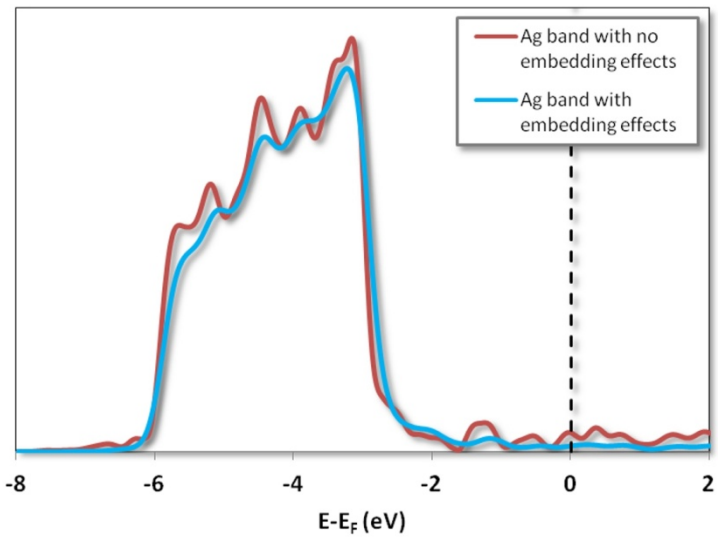


Table S1. Molecular parameters for all atomic species involved.

	ε (kJ·mol^{-1})	σ (Å)
Ag	19.0608	2.955
Si	1.0264	3.000
W	0.9250	2.340
O	0.8975	3.170
OW	0.6502	3.166
HW	0.0000	0.000
K	0.4187	3.332

References

1. B. Martorell, A. Clotet and J. Fraxedas, *J. Comput. Chem.*, 2010, **31**, 1842-1852.