Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Calculating the Adsorption Energy of a Charged Adsorbent in a Periodic Metallic System – The Case of BH_4^- Hydrolysis on Ag(111) Surface

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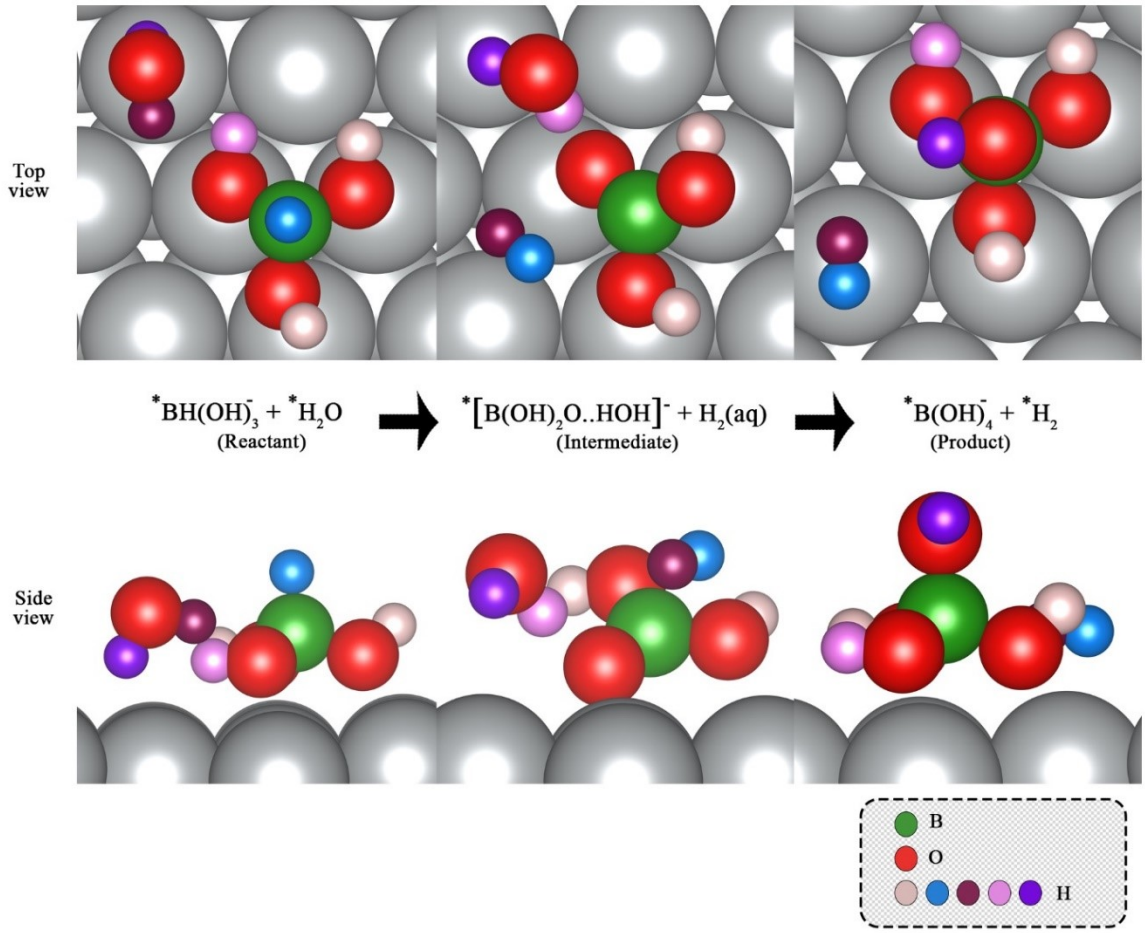

Figure S1*: Reaction mechanism of fourth step (reaction 9).*

Supplementary Data

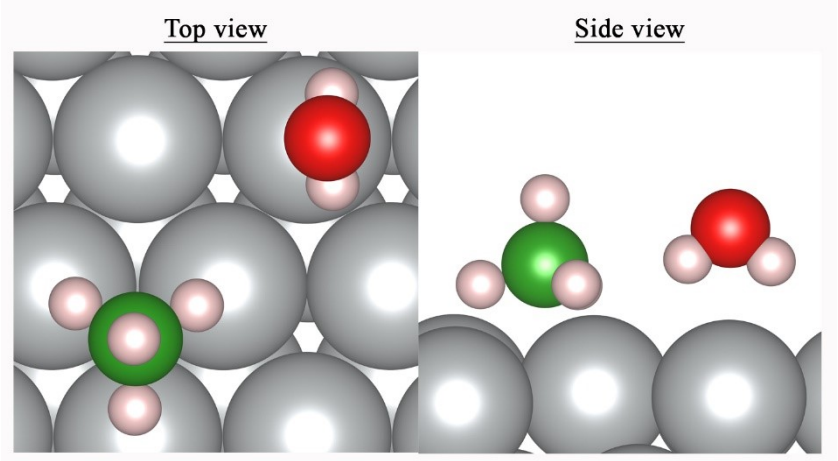

Figure S2: *Co-adsorbed structure of H_2O and BH_4^- on Ag(111) surface.*

Catalytic Cycle: Desorption of ions

$$^{*}BH_3(OH)^{-} + {}^{*}BH_4^{-} \rightarrow BH_3(OH)^{-}_{(aq)} + {}^{*}BH_4^{-} \quad \textbf{(S1)}$$

$$\Delta G^0 = -0.39\ eV$$

$$^{*}BH_3(OH)^{-} + {}^{*}BH_4^{-} \rightarrow {}^{*}BH_3(OH)^{-} + BH_{4(aq)}^{-} \quad \textbf{(S2)}$$

$$\Delta G^0 = -1.10\ eV$$

$$^{*}BH_2(OH)_2^{-} + {}^{*}BH_4^{-} \rightarrow BH_2(OH)_{2(aq)}^{-} + {}^{*}BH_4^{-} \quad \textbf{(S3)}$$

$$\Delta G^0 = -0.67\ eV$$

$$^{*}BH_2(OH)_2^{-} + {}^{*}BH_4^{-} \rightarrow {}^{*}BH_2(OH)_2^{-} + BH_{4(aq)}^{-} \quad \textbf{(S4)}$$

$$\Delta G^0 = -1.23\ eV$$

$$^{*}BH(OH)_2 + {}^{*}BH_4^{-} \rightarrow BH(OH)_{2(aq)} + {}^{*}BH_4^{-} \quad \textbf{(S5)}$$

$$\Delta G^0 = 0.26\ eV$$

$$^{*}BH(OH)_2 + {}^{*}BH_4^{-} \rightarrow {}^{*}BH(OH)_2 + BH_{4(aq)}^{-} \quad \textbf{(S6)}$$

$$\Delta G^0 = 0.48\ eV$$

$$^{*}BH(OH)_3^{-} + {}^{*}BH_4^{-} \rightarrow BH(OH)_{3(aq)}^{-} + {}^{*}BH_4^{-} \quad \textbf{(S7)}$$

$$\Delta G^0 = -0.58\ eV$$

$$^{*}BH(OH)_3^{-} + {}^{*}BH_4^{-} \rightarrow {}^{*}BH(OH)_3^{-} + BH_{4(aq)}^{-} \quad \textbf{(S8)}$$

$$\Delta G^0 = -1.13\ eV$$

$$^{*}B(OH)_4^- + {}^{*}BH_4^- \rightarrow B(OH)_{4(aq)}^- + {}^{*}BH_4^- \quad \textbf{(S9)}$$

$$\Delta G^0 = -0.56\ eV$$

$$^{*}B(OH)_4^- + {}^{*}BH_4^- \rightarrow {}^{*}B(OH)_4^- + BH_{4(aq)}^- \quad \textbf{(S10)}$$

$$\Delta G^0 = -1.05\ eV$$

$$^{*}BH\square\square_3(OH)^- + {}^{*}BH\square_2(OH)_2^- \rightarrow {}^{*}BH\square\square_3(OH)^- + BH_2(OH)_{2\,(aq)}^- \quad \textbf{(S11)}$$

$$\Delta G^0 = -0.700\ eV$$

$$^{*}BH\square\square_3(OH)^- + {}^{*}BH\square_2(OH)_2^- \rightarrow BH_3(OH)_{(aq)}^- + {}^{*}BH_2(OH)_2^- \quad \textbf{(S12)}$$

$$\Delta G^0 = -0.468\ eV$$

$$^{*}BH\square\square_3(OH)^- + {}^{*}BH(OH)_2 \rightarrow {}^{*}BH\square\square_3(OH)^- + BH(OH)_{2(aq)} \quad \textbf{(S13)}$$

$$\Delta G^0 = 0.429\ eV$$

$$^{*}BH\square\square_3(OH)^- + {}^{*}BH(OH)_2 \rightarrow BH_3(OH)_{(aq)}^- + {}^{*}BH(OH)_2 \quad \textbf{(S14)}$$

$$\Delta G^0 = 1.33\ eV$$

$$^{*}BH\square\square_3(OH)^- + {}^{*}BH(OH)_3^- \rightarrow {}^{*}BH\square\square_3(OH)^- + BH(OH)_{3\,(aq)}^- \quad \textbf{(S15)}$$

$$\Delta G^0 = -0.386\ eV$$

$$^{*}BH\square\square_3(OH)^- + {}^{*}BH(OH)_3^- \rightarrow BH_3(OH)_{(aq)}^- + {}^{*}BH(OH)_3^- \quad \textbf{(S16)}$$

$$\Delta G^0 = -0.212\ eV$$

$$^{*}BH_3(OH)^{-} + {}^{*}B(OH)_4^{-} \rightarrow {}^{*}BH_3(OH)^{-} + B(OH)_{4(aq)}^{-} \quad \textbf{(S17)}$$

$$\Delta G^0 = -0.63\ eV$$

$$^{*}BH_3(OH)^{-} + {}^{*}B(OH)_4^{-} \rightarrow BH_3(OH)_{(aq)}^{-} + {}^{*}B(OH)_4^{-} \quad \textbf{(S18)}$$

$$\Delta G^0 = -0.40\ eV$$