

a) **Aniline**



b) **Acetylacetonone (Hacac)**

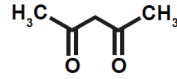
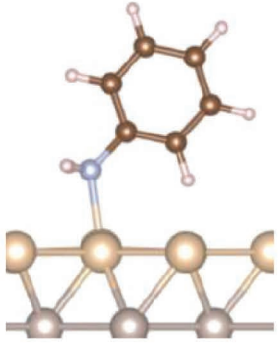


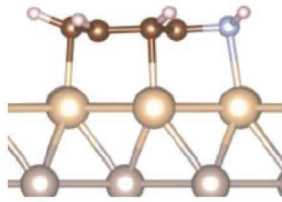
Figure 1: Illustrations showing the chemical structures of (a) aniline and (b) acetylacetonone (Hacac).

a) δ -bond



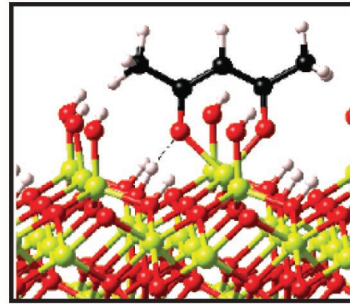
$$E_{\text{ads}} = -1.28 \text{ eV}$$

π -bond



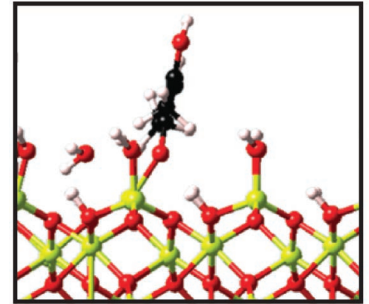
$$E_{\text{ads}} = -3.59 \text{ eV}$$

b) Chelate



$$E_{\text{ads}} = -0.99 \text{ eV}$$

Monodentate



$$E_{\text{ads}} = -0.82 \text{ eV}$$

Figure 2: Favorable adsorption configurations, as found by DFT calculations, for (a) aniline on Ru and (b) Hacac adsorption on Al_2O_3 including their adsorption energies. Because of the relatively low binding energy of Hacac in monodentate configuration it can desorb from the non-growth area.

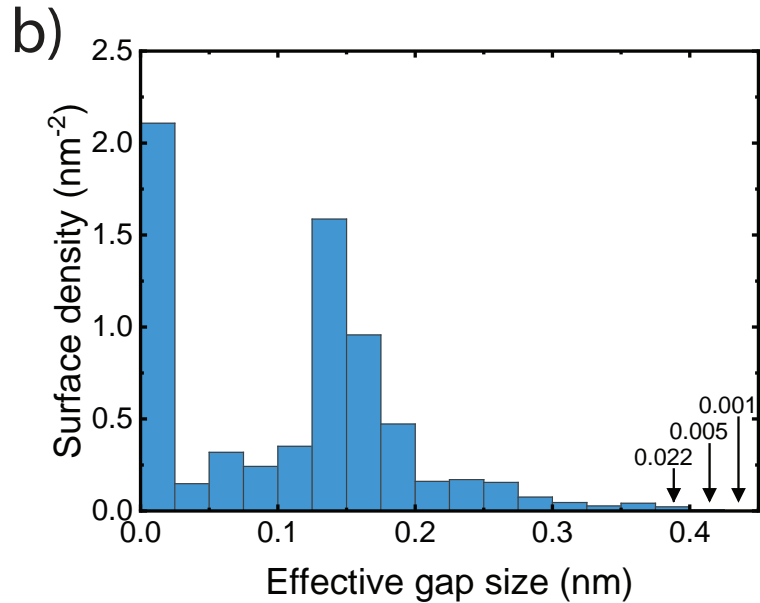
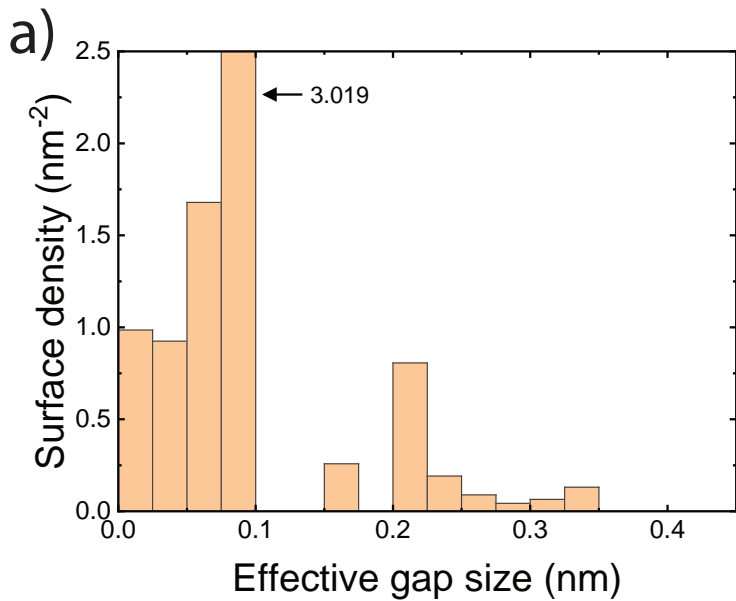


Figure 3: Random sequential adsorption simulation results for (a) aniline adsorption on Ru and (b) Hacac adsorption on Al_2O_3 . The reported effective gap size indicates the maximum size of a precursor molecule that would still fit in the gap. Whereas aniline leaves no gaps larger than 0.35 nm in radius in saturation, Hacac adsorption leads to gaps upto 0.45 nm in radius. To put these values in perspective, the ALD precursor tetrakis(dimethylamino)titanium (TDMAT) is ~ 0.5 nm in radius.