

Supplemental document

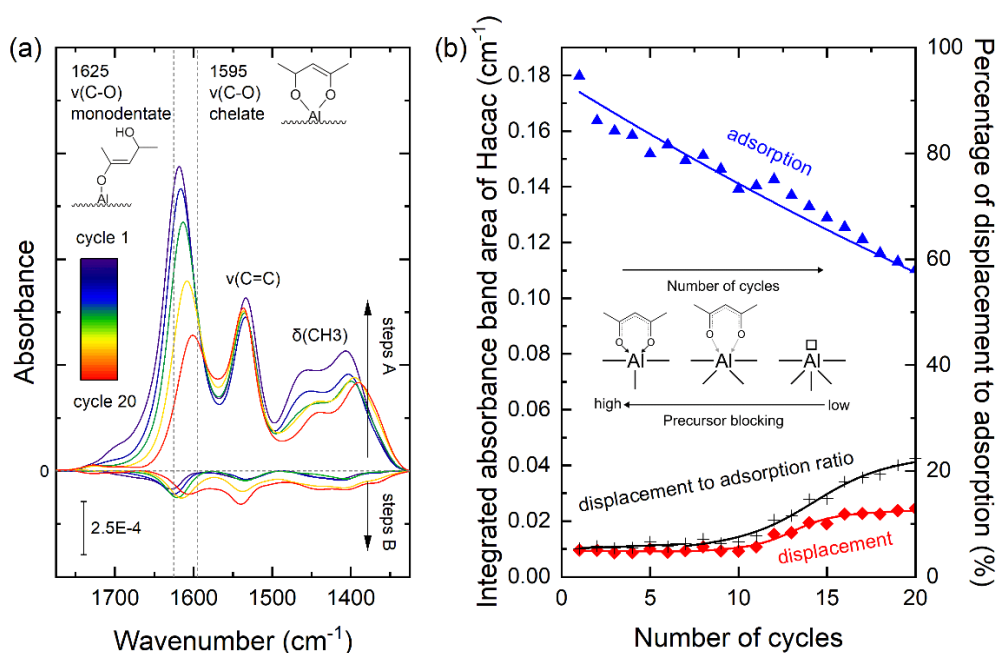


Figure 1. RAIRS measurement of ABDC-type AS-ALD of SiO₂ on Al₂O₃ as a function of cycles. (a) Difference spectra of steps A (Hacac doses, positive band) and steps B (BDEAS doses, negative band) using the prior spectrum as the reference. (b) The coverage of acac adsorbates in steps A decreases as a function of cycles (blue triangle). Part of the decrease in coverage can be attributed to the loss of the effective area of Al₂O₃ due to the formation of SiO₂ defects. Furthermore, the amount of acac adsorbates displaced in steps B increases as a function of cycles (red diamond). The ratio of displacement to adsorption shows that roughly 5% of the acac adsorbates were displaced in the first cycle, and the amount increased to roughly 22% after 20 cycles (dark dagger). This increasing trend of displacement suggests that the precursor (BDEAS) blocking of acac adsorbates decreases throughout the cycle. The red-shift (a) of the absorption band suggests a decrease in the ratio of monodentate to chelate bonding configuration of the acac adsorbates. The chelate form is known to be the effective configuration for blocking BDEAS. These two contradicting trends can be explained by the formation of highly coordinated Al surface species, as shown in the inset of (b), with the accumulation of the SiO₂ defects [4].

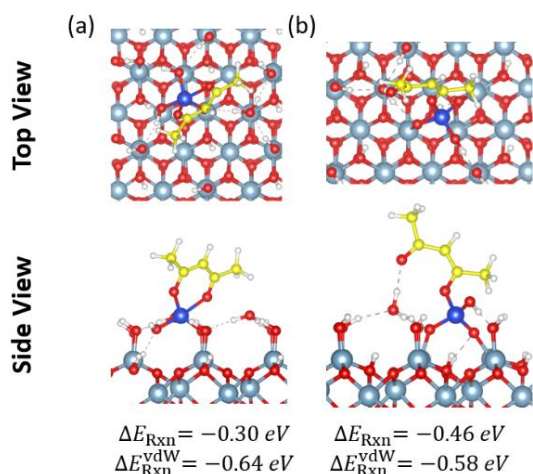


Figure 2. DFT calculations of adsorption of Hacac molecule to SiO₂ defect on α-Al₂O₃ (0001) surface. Two scenarios were considered: (a) SiO₂ defect with 3 OH groups, (b) SiO₂ defect with 2 OH groups. The results of both cases indicate that the Hacac molecule is not likely to chemisorb onto the SiO₂ defect.