**Table S2.** Molecular properties and heats of formation (at 0 K) of the stationary points on the Al(OH)2 + H potential energy surface. The geometries are illustrated in Figure 4c in the main paper.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molecule  (electronic state) | Geometry  (Cartesian co-ordinates in Å) a | Rotational constants  (GHz) a | Vibrational frequencies  (cm‑1) a | Δf*H*o(0 K)  (kJ mol-1) b |
| AlO  (2Σ+) | Al, 0., 0., -0.008  O, 0., 0., 1.623 | 18.916 | 946 c | 70 d |
| OAlO2  (2A2) | Al, 0., 0., -0.394  O, 0., -0.684, 1.318  O, 0., 0.685, 1.318  O, 0., 0., -1.994 | 33.702 4.0970 3.6530 | 189, 192, 454, 556, 1109, 1157 | -148 |
| TS from OAlO2 to AlO3  (TS1) | Al, 0.931, 0.120, 0.567  O, -0.537, 0.973, 0.744  O, -0.239, -1.084, 0.877  O, 2.621, 0.349, 0.253 | 14.560 4.8875 3.6592 | 339*i*, 183, 218, 645, 783, 987 | -83 |
| AlO3  (2B2) | Al, 0.432, 0.281, -0.002  O, 2.034, 0.951, 0.088  O, 0.257, -1.450, -0.057  O, -0.925, 1.370, -0.031 | 7.1732 6.7640 3.4813 | 170, 190, 256, 644, 859, 868 | -92 |
| AlO2 (cyclic)  (2A2) | Al, 0., 0., 1.010  O, 0., 0.673, -0.822  O, 0., -0.673,-0.822 | 34.8353 10.2871 7.9418 | 336, 504, 1180 | 32 |
| OAlO  (2Πg) | Al, 0.0, 0.072, -0.0  O, 1.653, 0.071, -0.0  O, -1.654, 0.072, 0.0 | 5.7786 | 183, 214, 773, 830 | -69 |
| AlO-CO2 | C, 1.432, 0.072, 0.043  O, 0.343, -0.213, -0.266  O, 2.522, 0.307, 0.344  Al, -1.125, 2.435, -0.230  O, 0.389, 2.863, 0.205 | 9.1531 2.0912 1.7023 | 37, 57, 64, 141, 650, 675, 944, 1360, 2394 | -342 |
| TS from AlO-CO2 to AlCO3  (TS1) | Al, 1.445, 0.820, -0.004  O, -0.736, 1.075, 0.049  C, -1.071, -0.074, 0.015  O, -1.662, -1.059, -0.008  O, 1.154, -0.797, -0.054 | 9.7093 3.2467 2.4331 | -223*i*, 116, 206, 281, 559, 655, 930, 1276, 2305 | -335 e |
| AlCO3  (3B1) | Al, 0.0, -1.589, 0.  O, -1.111, -0.219, 0.  C, -0.0, 0.605, 0.  O, 0.0, 1.792, 0.0  O, 1.111,-0.219, 0. | 12.789 4.1025 3.1061 | 189, 500, 577, 658, 794, 862, 911, 1016, 1862 | -480 |
| TS from AlO-CO2 to OAlO-CO  (TS2) | Al, 0.973, -0.3215, 0.0  O, -0.660, 0.937, 0.0  O, 2.537, 0.092, 0.0  C, -1.385, -0.0446, 0.0  O, -2.358, -0.671, 0.0 | 21.5321 2.03810 1.86187 | 383*i*, 86,  125, 185,  494, 511,  996, 1168,  2184 | -269 |
| OAlO-CO | Al, -0.891, -0.004, 0.0  O, 0.618, 0.996, 0.001  O, -2.463, -0.329, 0.002  C, 1.253, -0.148, 0.0  O, 2.35, -0.549, 0.0 | 22.2861 2.17845 1.98447 | 140, 155,  193, 366,  474, 725,  1039, 1112,  1925 | -314 |
|  |  |  |  |  |

aCalculated at the B3LYP/6-311+g(2d,p) level of theory 1

b Calculated at the CBS-QB3 level of theory,2 with reference values for Δf*H*o(Al) = 327.3 kJ mol-1, Δf*H*o(O) = 246.8 kJ mol-1, Δf*H*o(CO) = -113.8 kJ mol-1, Δf*H*o(CO2) = -393.2 kJ mol-1 and Δf*H*o(H2O) = -238.9 kJ mol-1 at 0 K. 3

c Experimental values: *r*e(Al-O) = 1.6179 Å; *ω*e = 979 cm-1 4

d Calculated using *D*0(AlO) = 502.8 kJ mol-1 determined with the very accurate W1BD complete basis set method.1

e RRKM fit of the barrier (see text in the main paper). The CBS-QB3 energy is 13 kJ mol-1 lower.