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


# Electronic Supplementary Information

# A Theoretical Investigation on the Role of Catalyst Support and Regioselectivity of Molecular Adsorption on a Metal Oxide Surface: NO Reduction on Cu/$\gamma$-alumina

Wataru Ota[a,b], Yasuro Kojima[b], Saburo Hosokawa[b,c], Kentaro Teramura[b,c], Tsunehiro Tanaka[b,c], Tohru Sato[a,b,c]*

[a] *Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8103, Japan*

[b] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*

[c] *Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8245, Japan*

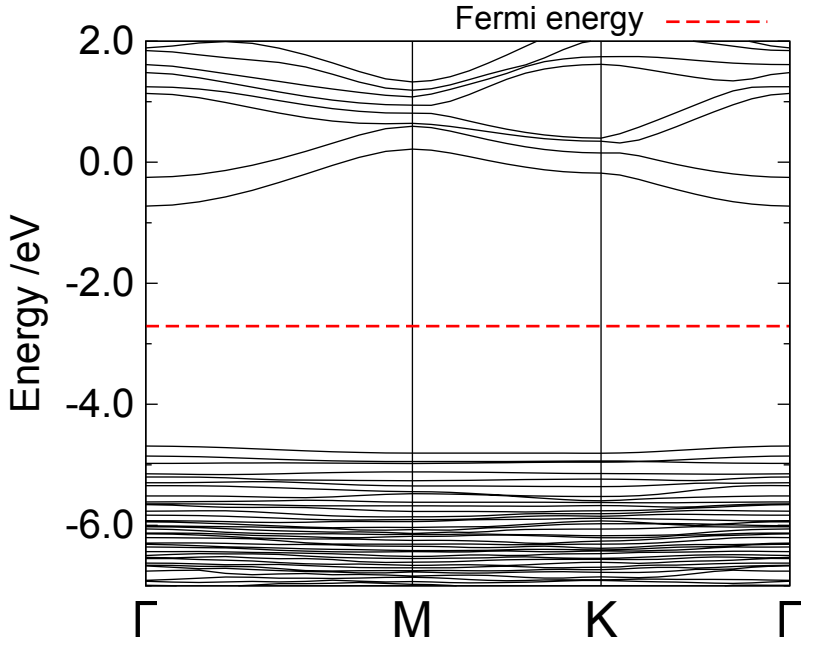


Figure S1. Calculated band structure of the SSHT slab model. The band gap is 3.97 eV.

Table S1. Cartesian coordinates of the SSHT slab model. Lattice vectors are (-8.0678, 0.0000, 0.0000) and (0.0000, 8.4130, 0.0000). The coordinates are provided in Angstrom units.

| No. | Atom | $x$ | $y$ | $z$ | No. | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Al | -0.8532 | -2.1445 | -0.5612 | 33 | O | 1.3434 | 3.4186 | -0.9256 |
| 2 | Al | 1.1183 | 2.1237 | 0.5174 | 34 | O | -1.0954 | -3.4306 | 0.9288 |
| 3 | Al | -3.9268 | 2.0726 | 1.9764 | 35 | O | -1.0606 | -0.8853 | 0.9367 |
| 4 | Al | -3.8845 | -2.1163 | -2.0309 | 36 | O | 1.3445 | 0.8895 | -0.9797 |
| 5 | Al | -0.7291 | -2.1526 | 2.3045 | 37 | O | 3.0706 | -0.7118 | -2.0428 |
| 6 | Al | 0.9851 | 2.1587 | -2.3391 | 38 | O | -2.7743 | 0.7033 | 1.9970 |
| 7 | Al | 2.1827 | -2.0494 | 0.6751 | 39 | O | -2.8279 | 3.4682 | 2.0617 |
| 8 | Al | -1.9200 | 2.1306 | -0.6751 | 40 | O | 3.0547 | -3.4826 | -2.0462 |
| 9 | Al | 3.2610 | 0.6592 | -0.8137 | 41 | O | 2.8364 | 2.0514 | 3.2291 |
| 10 | Al | -2.9661 | -0.6557 | 0.7554 | 42 | O | -2.6166 | -2.4034 | -3.2768 |
| 11 | Al | -2.9988 | -3.5769 | 0.7977 | 43 | O | -0.8803 | -3.5822 | 3.4350 |
| 12 | Al | 3.2391 | 3.5990 | -0.7783 | 44 | O | -0.7107 | -0.7036 | 3.4130 |
| 13 | Al | 1.1980 | -3.4664 | -2.1325 | 45 | O | 1.0240 | 0.7104 | -3.4290 |
| 14 | Al | -0.9425 | 3.4665 | 2.1387 | 46 | O | 1.1612 | 3.5945 | -3.4700 |
| 15 | Al | -0.8565 | 0.6350 | 2.0730 | 47 | O | 1.1027 | -2.0526 | -3.3691 |
| 16 | Al | 1.1586 | -0.6416 | -2.1244 | 48 | O | -0.8946 | 2.0340 | 3.3624 |
| 17 | O | 1.1042 | -2.4880 | 2.0387 | 49 | H | -0.8990 | -3.6873 | 4.4039 |
| 18 | O | -0.8358 | 2.4934 | -2.0475 | 50 | H | -0.1868 | -0.5600 | 4.2270 |
| 19 | O | 3.0532 | 2.1092 | 0.4986 | 51 | H | -1.6305 | 1.9482 | 4.0115 |
| 20 | O | -2.7804 | -2.1103 | -0.5342 | 52 | H | 1.2013 | -3.5711 | 2.0778 |
| 21 | O | 1.0544 | -2.0888 | -0.7611 | 53 | H | 3.8205 | 2.1588 | -2.8493 |
| 22 | O | -0.7881 | 2.0931 | 0.7454 | 54 | H | 1.0212 | 0.5948 | -4.3975 |
| 23 | O | 3.1987 | 2.1327 | -2.0858 | 55 | H | 0.3266 | -2.0683 | -3.9760 |
| 24 | O | -2.8919 | -2.1045 | 2.0757 | 56 | H | 2.9879 | 2.0437 | 4.2012 |
| 25 | O | 0.9815 | 3.4223 | 1.9889 | 57 | H | -2.7926 | -2.4397 | -4.2435 |
| 26 | O | -0.7320 | -3.4516 | -1.9971 | 58 | H | 1.6861 | 0.8258 | 2.5299 |
| 27 | O | -0.6912 | -0.7763 | -1.8274 | 59 | H | -3.4662 | -2.0932 | 2.8751 |
| 28 | O | 0.9784 | 0.7850 | 1.8281 | 60 | H | -0.9186 | 3.6123 | -2.0851 |
| 29 | O | 3.2683 | -0.6428 | 0.5749 | 61 | H | 1.7686 | 3.7268 | -4.2273 |
| 30 | O | -2.9337 | 0.6544 | -0.6651 | 62 | H | -1.4400 | -0.1669 | -2.0215 |
| 31 | O | -3.0102 | 3.5246 | -0.5532 | 63 | H | 1.6000 | 3.0011 | 2.6990 |
| 32 | O | 3.2518 | -3.4887 | 0.5769 | 64 | H | -1.4481 | -3.0488 | -2.6881 |

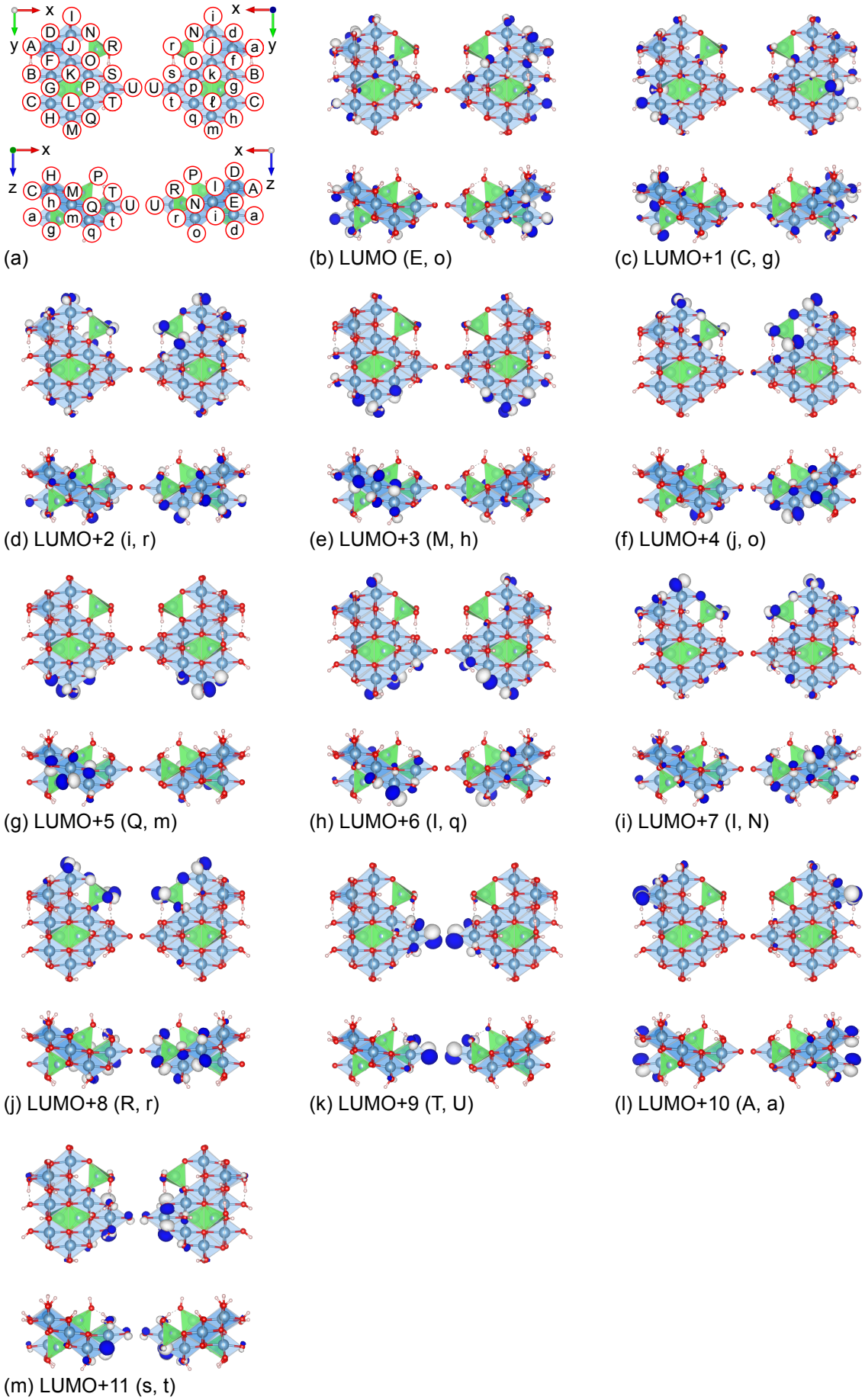


Figure S2. (a) Labels of O atoms of the bare cluster. (b)–(m) LUMO–LUMO+11 of the bare cluster. The O atoms that should be terminated by H atoms because of large molecular orbital coefficients are provided in parentheses. Isosurface values are $5.0 \times 10^{-2}$. a.u.

Table S2. Molecular orbital coefficients of the O atoms for the LUMO. The O atoms that should be terminated by H atoms are at E and o.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0098 | T | 0.0167 |
| B | 0.0129 | U | 0.0052 |
| C | 0.0461 | a | 0.0666 |
| D | 0.0053 | d | 0.0775 |
| E | 0.0402 | f | 0.0601 |
| F | 0.0018 | g | 0.0253 |
| G | 0.0007 | h | 0.0034 |
| H | 0.0365 | i | 0.0248 |
| I | 0.0216 | j | 0.0115 |
| J | 0.0012 | k | 0.0113 |
| K | 0.0155 | l | 0.0028 |
| L | 0.0057 | m | 0.0033 |
| M | 0.0046 | o | 0.0414 |
| N | 0.0040 | p | 0.0071 |
| O | 0.0128 | q | 0.0010 |
| P | 0.0041 | r | 0.0075 |
| Q | 0.0007 | s | 0.0259 |
| R | 0.0027 | t | 0.0030 |
| S | 0.0047 | | |

Table S3. Molecular orbital coefficients of the O atoms for the LUMO+1. The O atoms that should be terminated by H atoms are at C and g.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0177 | T | 0.0040 |
| B | 0.0409 | U | 0.0022 |
| C | 0.0817 | a | 0.0136 |
| D | 0.0010 | d | 0.0141 |
| E | 0.0272 | f | 0.0043 |
| F | 0.0014 | g | 0.0977 |
| G | 0.0007 | h | 0.0015 |
| H | 0.0683 | i | 0.0042 |
| I | 0.0206 | j | 0.0097 |
| J | 0.0004 | k | 0.0232 |
| K | 0.0048 | l | 0.0026 |
| L | 0.0119 | m | 0.0054 |
| M | 0.0126 | o | 0.0370 |
| N | 0.0039 | p | 0.0024 |
| O | 0.0092 | q | 0.0024 |
| P | 0.0006 | r | 0.0189 |
| Q | 0.0004 | s | 0.0126 |
| R | 0.0079 | t | 0.0006 |
| S | 0.0017 | | |

Table S4. Molecular orbital coefficients of the O atoms for the LUMO+2. The O atoms that should be terminated by H atoms are at i and r.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0115 | T | 0.0063 |
| B | 0.0049 | U | 0.0019 |
| C | 0.0036 | a | 0.0317 |
| D | 0.0202 | d | 0.0390 |
| E | 0.0159 | f | 0.0304 |
| F | 0.0014 | g | 0.0084 |
| G | 0.0003 | h | 0.0201 |
| H | 0.0101 | i | 0.0898 |
| I | 0.0386 | j | 0.0237 |
| J | 0.0026 | k | 0.0014 |
| K | 0.0001 | l | 0.0004 |
| L | 0.0013 | m | 0.0100 |
| M | 0.0234 | o | 0.0970 |
| N | 0.0155 | p | 0.0067 |
| O | 0.0049 | q | 0.0062 |
| P | 0.0006 | r | 0.0709 |
| Q | 0.0119 | s | 0.0229 |
| R | 0.0272 | t | 0.0011 |
| S | 0.0039 | | |

Table S5. Molecular orbital coefficients of the O atoms for the LUMO+3. The O atoms that should be terminated by H atoms are at M and h.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0072 | T | 0.0087 |
| B | 0.0174 | U | 0.0039 |
| C | 0.0343 | a | 0.0042 |
| D | 0.0008 | d | 0.0081 |
| E | 0.0042 | f | 0.0023 |
| F | 0.0004 | g | 0.0069 |
| G | 0.0007 | h | 0.1394 |
| H | 0.0192 | i | 0.0155 |
| I | 0.0005 | j | 0.0046 |
| J | 0.0004 | k | 0.0018 |
| K | 0.0002 | l | 0.0024 |
| L | 0.0019 | m | 0.0712 |
| M | 0.1054 | o | 0.0044 |
| N | 0.0024 | p | 0.0044 |
| O | 0.0000 | q | 0.0587 |
| P | 0.0001 | r | 0.0142 |
| Q | 0.0988 | s | 0.0072 |
| R | 0.0052 | t | 0.0053 |
| S | 0.0009 | | |

Table S6. Molecular orbital coefficients of the O atoms for the LUMO+4. The O atoms that should be terminated by H atoms are at j and o.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0018 | T | 0.0033 |
| B | 0.0007 | U | 0.0078 |
| C | 0.0005 | a | 0.0001 |
| D | 0.0086 | d | 0.0015 |
| E | 0.0320 | f | 0.0003 |
| F | 0.0001 | g | 0.0014 |
| G | 0.0001 | h | 0.0014 |
| H | 0.0006 | i | 0.1389 |
| I | 0.0449 | j | 0.0473 |
| J | 0.0002 | k | 0.0083 |
| K | 0.0014 | l | 0.0002 |
| L | 0.0000 | m | 0.0005 |
| M | 0.0011 | o | 0.1911 |
| N | 0.0470 | p | 0.0011 |
| O | 0.0091 | q | 0.0017 |
| P | 0.0004 | r | 0.0664 |
| Q | 0.0004 | s | 0.0253 |
| R | 0.0174 | t | 0.0003 |
| S | 0.0018 | | |

Table S7. Molecular orbital coefficients of the O atoms for the LUMO+5. The O atoms that should be terminated by H atoms are at Q and m.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0003 | T | 0.0060 |
| B | 0.0007 | U | 0.0009 |
| C | 0.0007 | a | 0.0003 |
| D | 0.0003 | d | 0.0001 |
| E | 0.0003 | f | 0.0001 |
| F | 0.0001 | g | 0.0022 |
| G | 0.0005 | h | 0.1387 |
| H | 0.0098 | i | 0.0014 |
| I | 0.0020 | j | 0.0004 |
| J | 0.0000 | k | 0.0000 |
| K | 0.0000 | l | 0.0028 |
| L | 0.0081 | m | 0.2935 |
| M | 0.0682 | o | 0.0006 |
| N | 0.0003 | p | 0.0009 |
| O | 0.0004 | q | 0.0213 |
| P | 0.0001 | r | 0.0006 |
| Q | 0.1079 | s | 0.0002 |
| R | 0.0003 | t | 0.0002 |
| S | 0.0001 | | |

Table S8. Molecular orbital coefficients of the O atoms for the LUMO+6. The O atoms that should be terminated by H atoms are at I and q.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0014 | T | 0.0410 |
| B | 0.0001 | U | 0.0040 |
| C | 0.0030 | a | 0.0106 |
| D | 0.0114 | d | 0.0019 |
| E | 0.0134 | f | 0.0006 |
| F | 0.0005 | g | 0.0007 |
| G | 0.0000 | h | 0.0136 |
| H | 0.0022 | i | 0.0153 |
| I | 0.0640 | j | 0.0109 |
| J | 0.0005 | k | 0.0003 |
| K | 0.0004 | l | 0.0051 |
| L | 0.0022 | m | 0.0965 |
| M | 0.0051 | o | 0.0092 |
| N | 0.0039 | p | 0.0036 |
| O | 0.0007 | q | 0.2677 |
| P | 0.0009 | r | 0.0045 |
| Q | 0.0186 | s | 0.0046 |
| R | 0.0014 | t | 0.0484 |
| S | 0.0006 | | |

Table S9. Molecular orbital coefficients of the O atoms for the LUMO+7. The O atoms that should be terminated by H atoms are at I and N.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0129 | T | 0.0148 |
| B | 0.0111 | U | 0.0030 |
| C | 0.0054 | a | 0.0290 |
| D | 0.0381 | d | 0.0009 |
| E | 0.0311 | f | 0.0041 |
| F | 0.0013 | g | 0.0014 |
| G | 0.0002 | h | 0.0112 |
| H | 0.0012 | i | 0.0336 |
| I | 0.1882 | j | 0.0205 |
| J | 0.0020 | k | 0.0003 |
| K | 0.0006 | l | 0.0011 |
| L | 0.0008 | m | 0.0203 |
| M | 0.0075 | o | 0.0145 |
| N | 0.0416 | p | 0.0018 |
| O | 0.0002 | q | 0.0477 |
| P | 0.0005 | r | 0.0657 |
| Q | 0.0039 | s | 0.0012 |
| R | 0.0344 | t | 0.0161 |
| S | 0.0002 | | |

Table S10. Molecular orbital coefficients of the O atoms for the LUMO+8. The O atoms that should be terminated by H atoms are at R and r.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0037 | T | 0.0002 |
| B | 0.0018 | U | 0.0014 |
| C | 0.0011 | a | 0.0009 |
| D | 0.0158 | d | 0.0039 |
| E | 0.0073 | f | 0.0009 |
| F | 0.0003 | g | 0.0010 |
| G | 0.0000 | h | 0.0018 |
| H | 0.0000 | i | 0.1519 |
| I | 0.0716 | j | 0.0085 |
| J | 0.0010 | k | 0.0028 |
| K | 0.0003 | l | 0.0002 |
| L | 0.0003 | m | 0.0050 |
| M | 0.0011 | o | 0.0497 |
| N | 0.0801 | p | 0.0010 |
| O | 0.0054 | q | 0.0147 |
| P | 0.0000 | r | 0.1532 |
| Q | 0.0013 | s | 0.0034 |
| R | 0.0820 | t | 0.0007 |
| S | 0.0003 | | |

Table S11. Molecular orbital coefficients of the O atoms for the LUMO+9. The O atoms that should be terminated by H atoms are at T and U.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0002 | T | 0.0498 |
| B | 0.0000 | U | 0.4328 |
| C | 0.0001 | a | 0.0005 |
| D | 0.0002 | d | 0.0001 |
| E | 0.0004 | f | 0.0000 |
| F | 0.0000 | g | 0.0001 |
| G | 0.0000 | h | 0.0005 |
| H | 0.0001 | i | 0.0003 |
| I | 0.0001 | j | 0.0010 |
| J | 0.0000 | k | 0.0004 |
| K | 0.0001 | l | 0.0009 |
| L | 0.0004 | m | 0.0039 |
| M | 0.0003 | o | 0.0045 |
| N | 0.0003 | p | 0.0008 |
| O | 0.0015 | q | 0.0128 |
| P | 0.0093 | r | 0.0053 |
| Q | 0.0012 | s | 0.0055 |
| R | 0.0108 | t | 0.0211 |
| S | 0.1069 | | |

Table S12. Molecular orbital coefficients of the O atoms for the LUMO+10. The O atoms that should be terminated by H atoms are at A and a.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.1702 | T | 0.0017 |
| B | 0.0057 | U | 0.0001 |
| C | 0.0006 | a | 0.3280 |
| D | 0.0248 | d | 0.0485 |
| E | 0.0013 | f | 0.0213 |
| F | 0.0042 | g | 0.0020 |
| G | 0.0000 | h | 0.0003 |
| H | 0.0001 | i | 0.0152 |
| I | 0.0247 | j | 0.0016 |
| J | 0.0003 | k | 0.0008 |
| K | 0.0002 | l | 0.0001 |
| L | 0.0000 | m | 0.0009 |
| M | 0.0002 | o | 0.0004 |
| N | 0.0047 | p | 0.0012 |
| O | 0.0003 | q | 0.0022 |
| P | 0.0000 | r | 0.0015 |
| Q | 0.0004 | s | 0.0097 |
| R | 0.0011 | t | 0.0114 |
| S | 0.0003 | | |

Table S13. Molecular orbital coefficients of the O atoms for the LUMO+11. The O atoms that should be terminated by H atoms are at s and t.

| O-label | Coefficient | O-label | Coefficient |
|---|---|---|---|
| A | 0.0072 | T | 0.0296 |
| B | 0.0001 | U | 0.0313 |
| C | 0.0001 | a | 0.0131 |
| D | 0.0012 | d | 0.0022 |
| E | 0.0003 | f | 0.0008 |
| F | 0.0004 | g | 0.0001 |
| G | 0.0000 | h | 0.0008 |
| H | 0.0002 | i | 0.0009 |
| I | 0.0013 | j | 0.0006 |
| J | 0.0004 | k | 0.0015 |
| K | 0.0005 | l | 0.0013 |
| L | 0.0004 | m | 0.0073 |
| M | 0.0006 | o | 0.0108 |
| N | 0.0017 | p | 0.0208 |
| O | 0.0036 | q | 0.0279 |
| P | 0.0006 | r | 0.0169 |
| Q | 0.0065 | s | 0.2214 |
| R | 0.0045 | t | 0.2472 |
| S | 0.0238 | | |

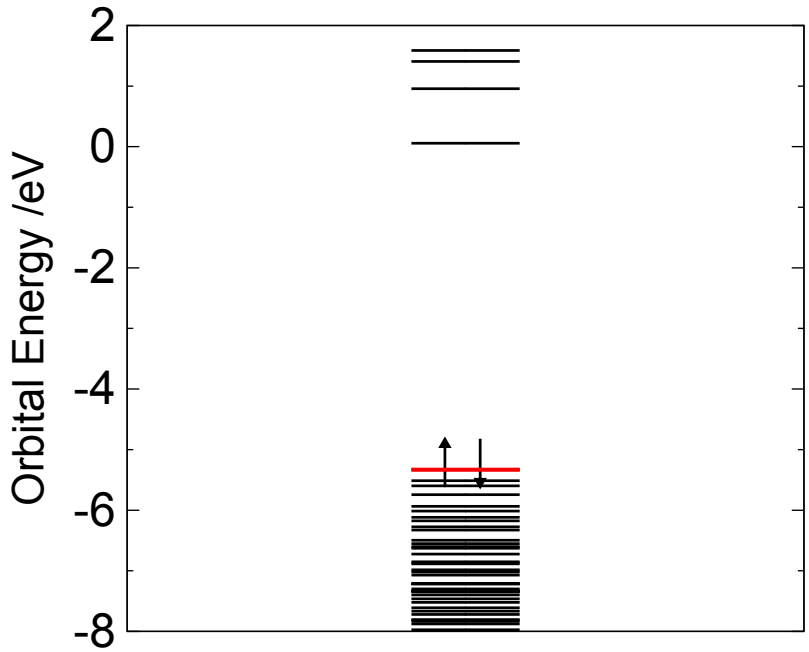


Figure S3. Calculated orbital levels of the SSHT cluster model. The energy gap is 5.39 eV.

Table S14. Cartesian coordinates of the SSHT cluster model. The coordinates are provided in Angstrom units.

| No. | Atom | $x$ | $y$ | $z$ | No. | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Al | -2.5502 | 3.0942 | -0.8695 | 48 | O | 5.2249 | 1.8849 | 1.2792 |
| 2 | Al | 3.2166 | -1.2169 | 1.6664 | 49 | O | -4.6889 | 0.8051 | 2.4615 |
| 3 | Al | -1.5393 | -0.0745 | -1.3152 | 50 | O | 5.3589 | 1.2095 | -1.4670 |
| 4 | Al | 3.4200 | -1.3881 | -1.2848 | 51 | O | -5.1650 | -1.4838 | 1.7196 |
| 5 | Al | -1.0325 | -1.1988 | 1.6144 | 52 | O | -4.4465 | 0.2456 | -0.1377 |
| 6 | Al | 1.7267 | 3.4648 | -0.4740 | 53 | O | -3.2238 | 4.6504 | -1.4638 |
| 7 | Al | 4.1619 | 1.2338 | -0.0048 | 54 | H | -0.3025 | 3.4943 | -2.2320 |
| 8 | Al | -3.9027 | -1.5183 | 0.3049 | 55 | H | 3.3814 | -3.7740 | -1.2575 |
| 9 | Al | -3.3571 | 1.0729 | 1.1627 | 56 | H | 1.6778 | -1.5870 | -3.1003 |
| 10 | Al | -0.6281 | 1.9749 | 1.0517 | 57 | H | -3.0948 | 1.4581 | -2.7084 |
| 11 | Al | 1.2776 | 0.2910 | 0.0178 | 58 | H | -1.2750 | -5.7087 | -0.6665 |
| 12 | Al | 0.7433 | -2.2661 | -0.9075 | 59 | H | 2.4161 | -1.2264 | 3.8830 |
| 13 | Al | -1.8693 | -3.2133 | -0.6837 | 60 | H | -1.2305 | 2.1810 | -2.8075 |
| 14 | O | -0.4508 | -1.7859 | 3.2118 | 61 | H | 1.7527 | -3.9919 | 0.4531 |
| 15 | O | 1.1962 | 4.0541 | -2.0353 | 62 | H | 0.8763 | -1.6662 | 3.1542 |
| 16 | O | 4.0528 | -3.1077 | -0.9378 | 63 | H | 4.4182 | -3.3290 | 2.1297 |
| 17 | O | 2.7527 | 0.7012 | 1.2228 | 64 | H | 2.6147 | 0.9433 | -2.0955 |
| 18 | O | -1.9346 | 1.3556 | -0.2431 | 65 | H | -0.0233 | 3.1316 | 3.2074 |
| 19 | O | -0.5662 | -2.3646 | 0.3723 | 66 | H | 0.1691 | -4.6243 | -0.3052 |
| 20 | O | 2.8207 | 0.5138 | -1.2330 | 67 | H | -0.7992 | -2.6022 | 3.6363 |
| 21 | O | -5.0136 | -2.4729 | -0.9316 | 68 | H | -5.3616 | -1.8834 | -1.6464 |
| 22 | O | -2.0283 | 1.8322 | 2.3045 | 69 | H | 1.7379 | 5.5453 | 0.9977 |
| 23 | O | 1.9749 | -1.4832 | 3.0373 | 70 | H | 5.2130 | -1.4785 | -3.0162 |
| 24 | O | -1.2246 | 3.0410 | -2.2778 | 71 | H | 6.1809 | 1.6539 | 1.3343 |
| 25 | O | 1.3252 | -4.0322 | -0.4446 | 72 | H | -4.2572 | -3.2741 | -1.4077 |
| 26 | O | -3.7172 | 2.0835 | -2.1075 | 73 | H | -5.4722 | 1.4035 | 2.3806 |
| 27 | O | -0.9863 | -4.8499 | -0.2816 | 74 | H | -3.3846 | -3.8344 | 1.3581 |
| 28 | O | 4.4445 | -0.7267 | 2.8799 | 75 | H | -0.3270 | -3.6149 | -2.7614 |
| 29 | O | -2.6935 | -0.6290 | 1.4533 | 76 | H | 5.1581 | 0.2420 | -2.1452 |
| 30 | O | 3.4820 | 2.9984 | -0.3267 | 77 | H | 2.4791 | 1.2776 | 1.9776 |
| 31 | O | 0.8436 | 2.0471 | -0.0863 | 78 | H | -1.8570 | 0.0726 | -3.7532 |
| 32 | O | -0.0033 | 0.2405 | 1.3385 | 79 | H | 4.0737 | 3.5486 | 0.2505 |
| 33 | O | 2.1207 | -1.4103 | 0.1288 | 80 | H | 4.8517 | 0.1673 | 2.7492 |
| 34 | O | -1.2723 | 3.6264 | 0.3936 | 81 | H | -4.5038 | 0.7685 | -0.9782 |
| 35 | O | -3.8041 | 2.8138 | 0.5731 | 82 | H | -5.0325 | -0.4170 | 2.2211 |
| 36 | O | 4.4883 | -0.6683 | 0.1399 | 83 | H | -3.0618 | -3.6900 | -2.7464 |
| 37 | O | -3.1081 | -3.1683 | 0.7013 | 84 | H | 0.9085 | 3.7835 | 1.9153 |
| 38 | O | -2.5618 | -1.4750 | -1.0319 | 85 | H | 5.5914 | 2.0413 | -1.9385 |
| 39 | O | 0.1992 | -0.4509 | -1.2645 | 86 | H | 1.4333 | 4.8380 | -2.5729 |
| 40 | O | -1.9214 | 0.6541 | -2.9605 | 87 | H | -1.9424 | 1.2946 | 3.1263 |
| 41 | O | 4.6498 | -0.8188 | -2.5521 | 88 | H | -3.9527 | 5.0606 | -0.9370 |
| 42 | O | -3.2263 | -3.9387 | -1.8010 | 89 | H | -4.2246 | 2.7701 | -2.6092 |
| 43 | O | 2.0495 | -2.0500 | -2.3176 | 90 | H | 5.4101 | -0.9795 | 0.2964 |
| 44 | O | -0.5691 | -2.9512 | -2.0781 | 91 | H | 4.0413 | -3.1975 | 0.2902 |
| 45 | O | 3.7946 | -2.9858 | 1.4495 | 92 | H | -3.6800 | 3.4878 | 1.2846 |
| 46 | O | 0.4584 | 2.9261 | 2.3711 | 93 | H | -0.8927 | 4.5192 | 0.5244 |
| 47 | O | 1.4592 | 4.6146 | 0.8687 | 94 | H | -6.1008 | -1.6834 | 1.4785 |

Table S15. OVCCs for the effective mode of the $\gamma$-alumina cluster model. The core orbitals are neglected.

| $i$ | | Energy / eV | $f_{i,\xi} \times 10^{-3}$ a.u. |
|---|---|---|---|
| 265 | HOMO | -5.921 | 1.525 |
| 263 | HOMO-2 | -8.861 | 1.052 |
| 264 | HOMO-1 | -8.978 | 1.038 |
| 260 | HOMO-5 | -9.161 | 0.840 |
| ⋮ | ⋮ | ⋮ | ⋮ |
| 149 | HOMO-116 | -17.613 | 0.007 |

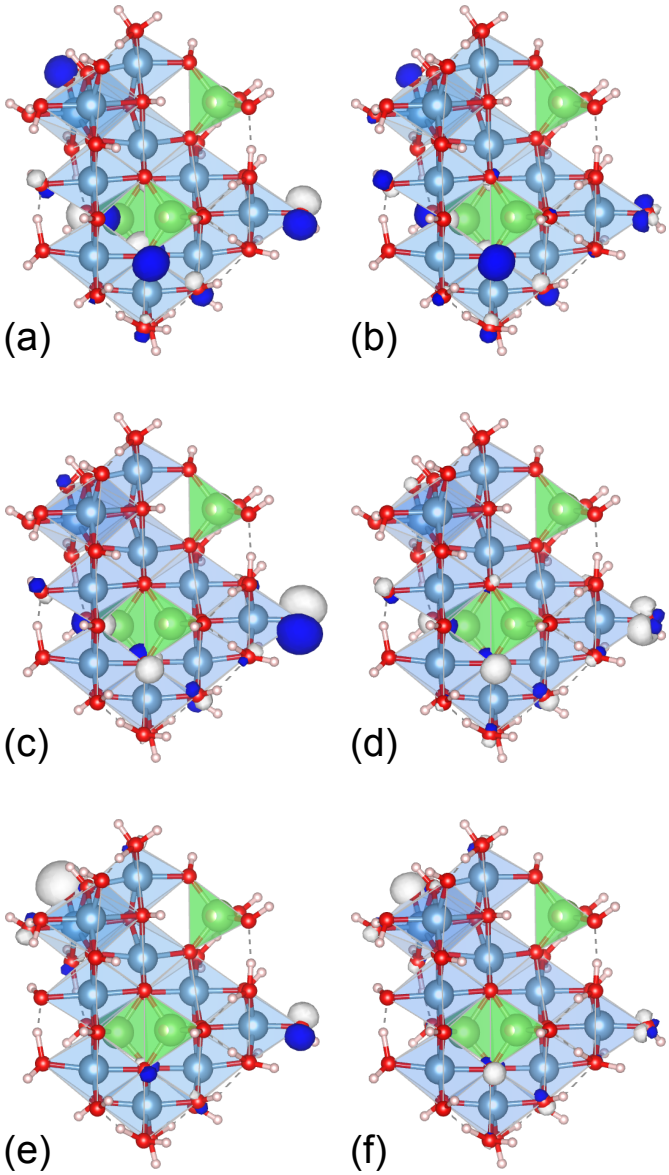


Figure S4. (a) HOMO, (b) OVCD for the HOMO, (c) HOMO-2, (d) OVCD for the HOMO-2, (e) HOMO-1, and (f) OVCD for the HOMO-1 of the $\gamma$-alumina cluster model. Isosurface values of the molecular orbitals are $5.0 \times 10^{-2}$ a.u., and of the OVCDs are $2.0 \times 10^{-5}$ a.u.

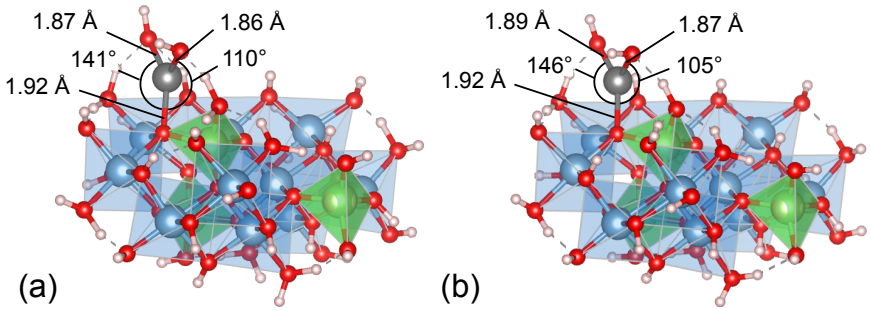


Figure S5. Geometry-optimized structures of the $Cu(OH)_2/\gamma$-alumina cluster model using the (a) 3-21G and (b) 6-31G(d,p) basis sets. The Cu–O distances and O–Cu–O angles are also shown.

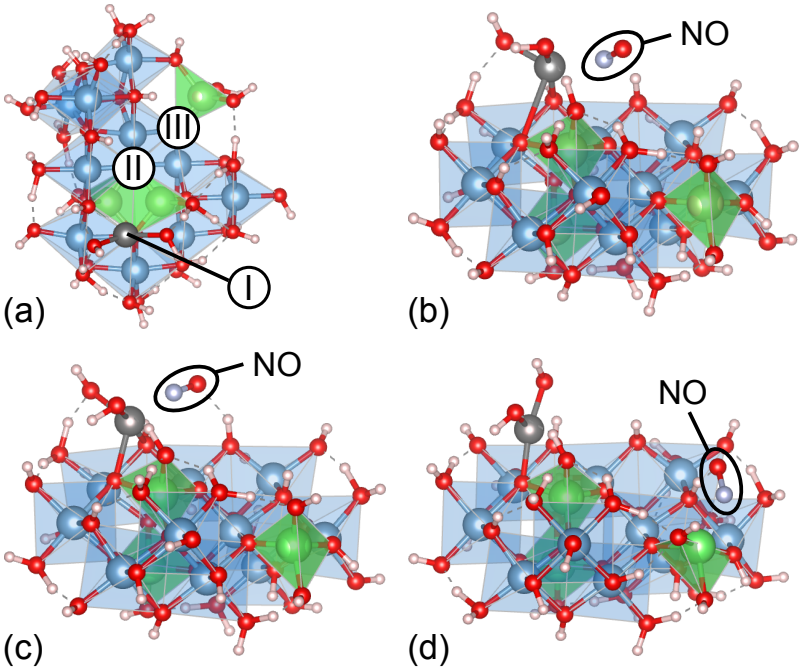


Figure S6. (a) Initial positions of NO on the $Cu(OH)_2/\gamma$-alumina cluster model. Geometry-optimized structures obtained by initially placing NO on positions (b) I, (c), II, or (d) III. The total energies of (c) and (d) respectively are 0.261 and 1.416 eV higher than that of (b). The reference of the total energy is that of (b), -8068.23720195 a.u.

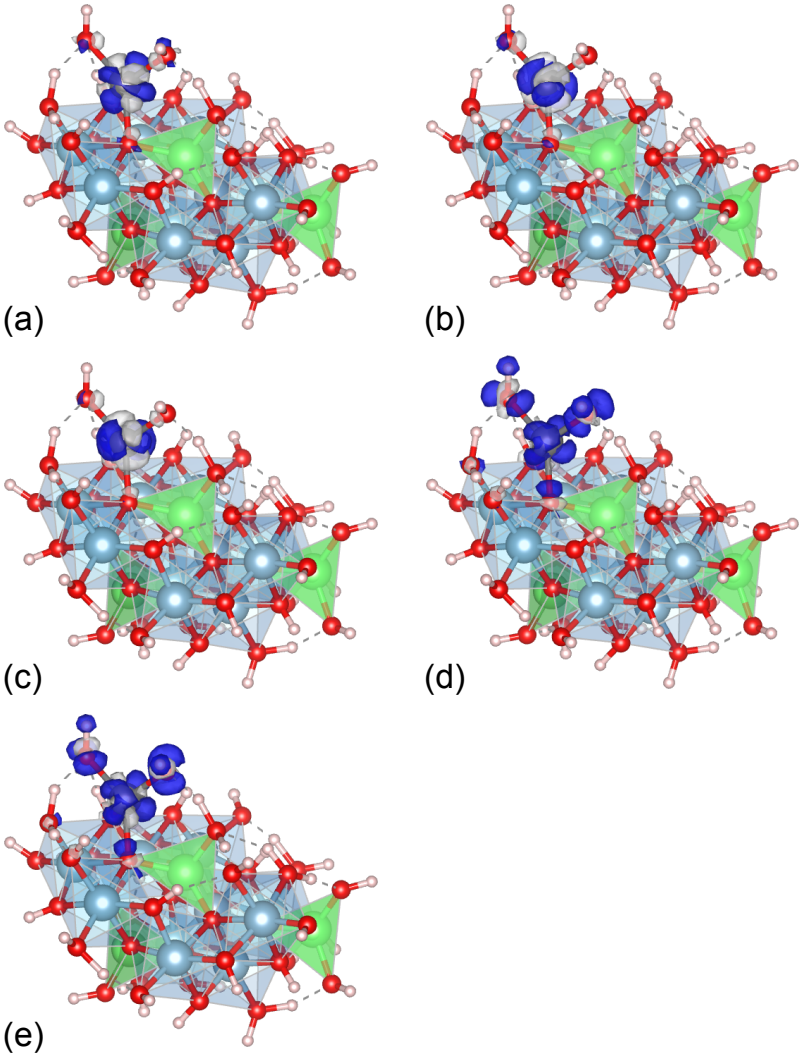


Figure S7. Electron density differences of the $Cu(OH)_2/\gamma$-alumina cluster model between (a) $S_1$ and $S_0$, (b) $S_2$ and $S_0$, (c) $S_4$ and $S_0$, (d) $S_6$ and $S_0$, and (e) $S_{12}$ and $S_0$. Isosurface values are $5.0 \times 10^{-3}$ a.u.

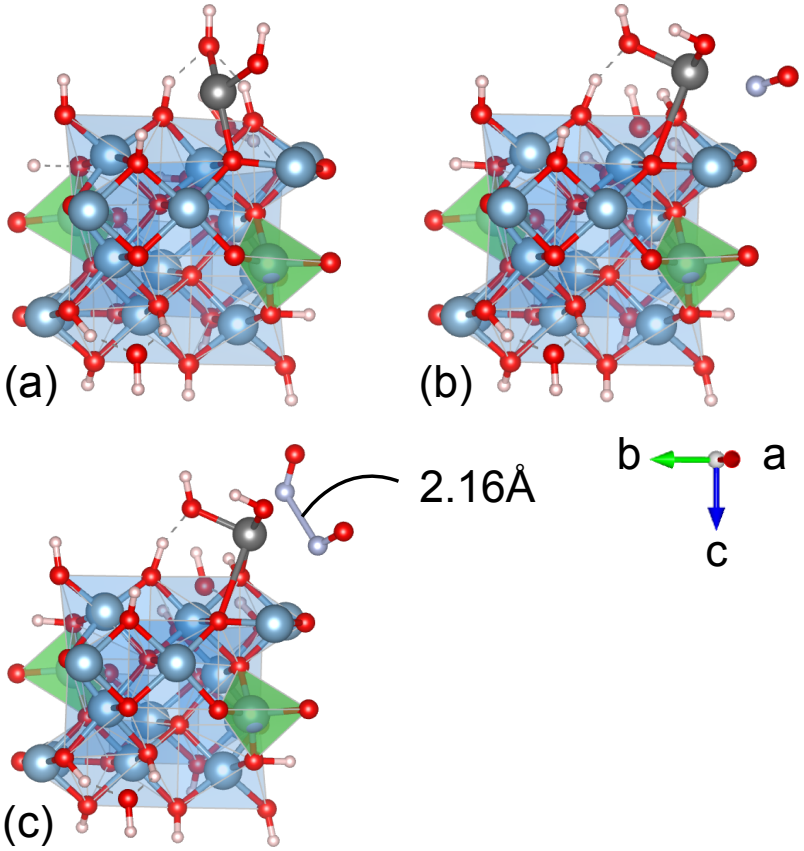


Figure S8. Geometry-optimized structures of the (a) $Cu(OH)_2/\gamma$-alumina, (b) NO-adsorbed $Cu(OH)_2/\gamma$-alumina, and (c) $(NO)_2$-adsorbed $Cu(OH)_2/\gamma$-alumina slab models.

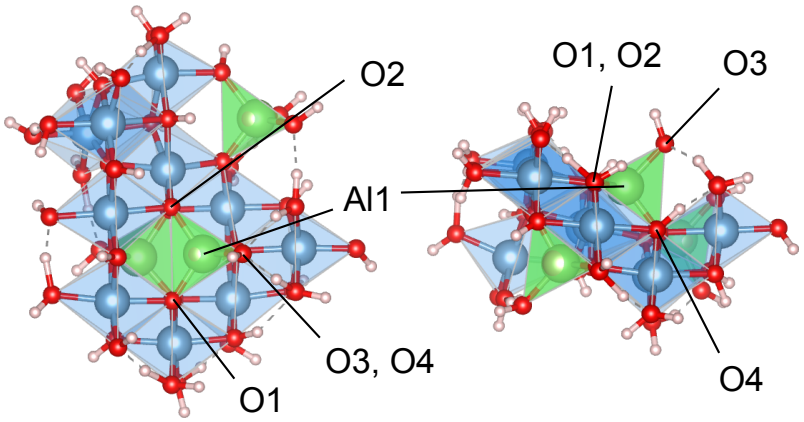


Figure S9. Atomic labels of the tetrahedral Al species on which $Cu(OH)_2$ is adsorbed.

Table S16. Interatomic distance and Mulliken charge of the tetrahedral Al species in Fig. S8 before and after the Cu adsorption.

| | | $d$ (Å) | | | | Mulliken charge | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Al1-O1 | Al1-O2 | Al1-O3 | Al1-O4 | Al1 | O1 | O2 | O3 | O4 |
| Cluster model | $\gamma$-alumina | 1.757 | 1.779 | 1.839 | 1.830 | 0.928 | -0.876 | -0.860 | -0.723 | -0.920 |
| | Cu/$\gamma$-alumina | 1.823 | 1.775 | 1.819 | 1.804 | 1.043 | -0.877 | -0.864 | -0.799 | -0.935 |
| Slab model | $\gamma$-alumina | 1.791 | 1.772 | 1.800 | 1.859 | 1.311 | -1.004 | -1.017 | -0.931 | -1.008 |
| | Cu/$\gamma$-alumina | 1.845 | 1.753 | 1.785 | 1.837 | 1.436 | -0.898 | -1.026 | -0.948 | -1.018 |

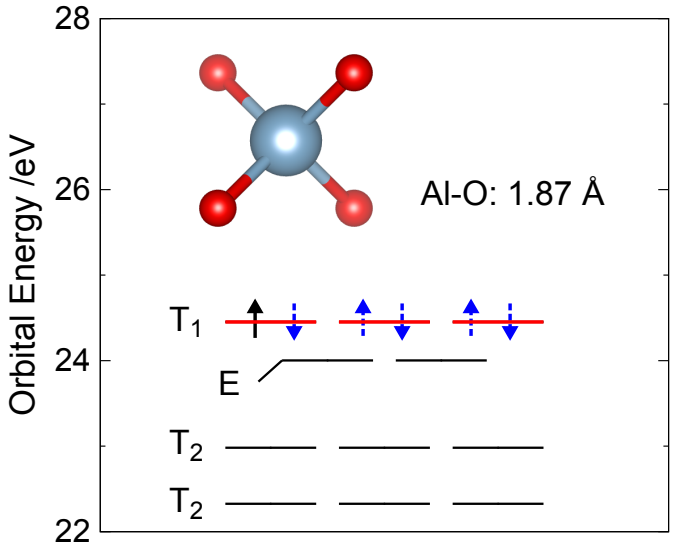


Figure S10. Orbital levels of the geometry-optimized $AlO_4$ with the $T_d$ symmetry. Five electrons are provided to obtain the appropriate oxidation number.

Table S17. VCCs of $AlO_4$.

| | Frequency ($cm^{-1}$) | VCC ($10^{-4}$ a.u.) |
|---|---|---|
| $e$ | 267.1 | 0.0000 |
| $t_2$ | 336.0 | 0.8621 |
| $a_1$ | 509.0 | 2.1265 |
| $t_2$ | 582.9 | 1.1002 |

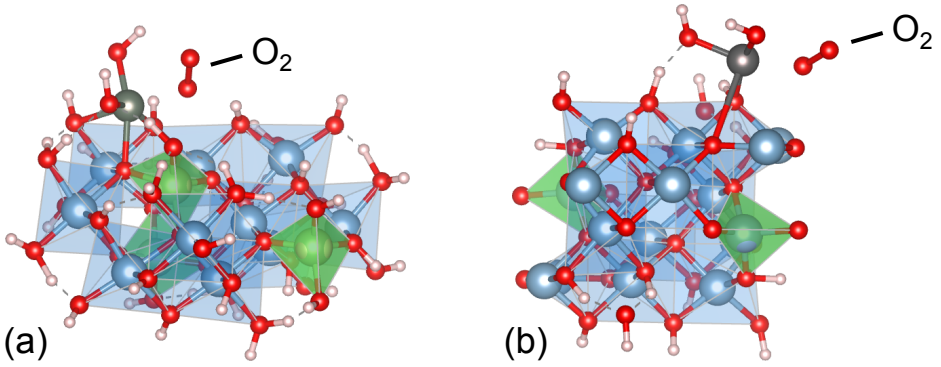


Figure S11. Geometry-optimized structures of the $O_2$-adsorbed $Cu(OH)_2/\gamma$-alumina (a) cluster and (b) slab models.

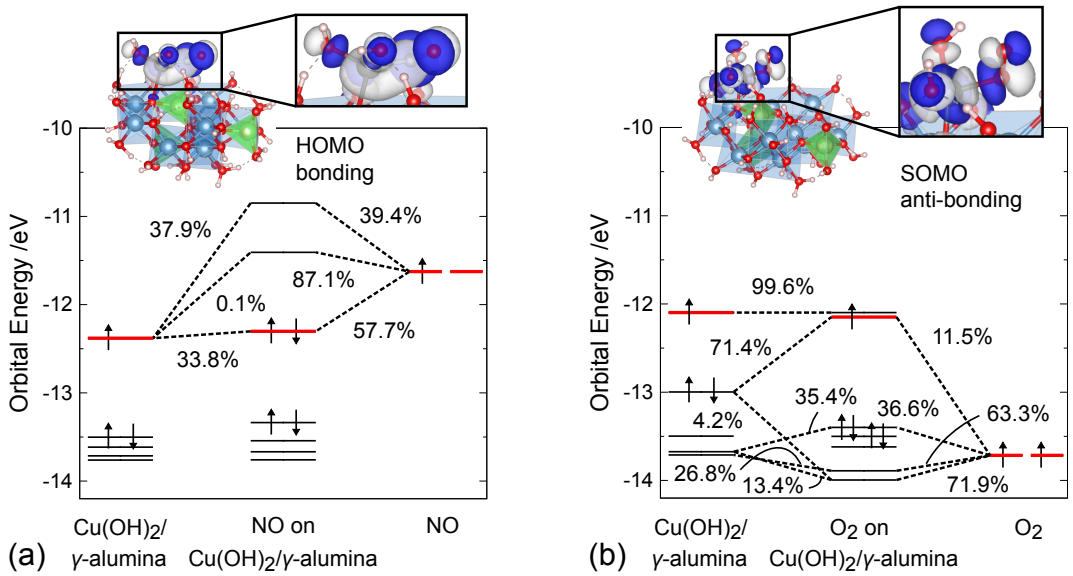


Figure S12. Fragment orbital analyses of the (a) NO- and (b) $O_2$-adsorbed $Cu(OH)_2/\gamma$-alumina cluster models. Values of $P_{km}$ are provided in percentages.