# Supporting Information

## Theoretical Study about $Mo_2C$(101)-Catalyzed Hydrodeoxygenation of Butyric Acid to Butane for Biomass Conversion

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**Table S1.** Influence of relaxed-layer thickness on adsorption energies on the clean *p*(2×2) surface (in eV, nR/mL, n for relaxed layers, and m for total layers; the ZPE corrected adsorption energies are given in parenthesis)

| | 1R/4L | 2R/4L | 3R/4L |
|---|---|---|---|
| R-CO | -3.28 (-3.22) | -3.29 (-3.23) | -3.28 (-3.22) |
| R-$CH_2O$ | -4.40 (-4.34) | -4.40 (-4.34) | -4.41 (-4.35) |
| R-$CH_2$ | -2.84 (-2.76) | -2.85 (-2.77) | -2.82 (-2.74) |

**Table S2.** Test calculations for the choice of vacuum thickness for the perpendicular adsorption of butyric acid on the clean *p*(2×2) surface

| Vacuum/ Å | $E_{ads}$/ eV |
|---|---|
| 12 | -0.47 |
| 15 | -0.89 |
| 17 | -0.91 |
| 20 | -0.91 |

**Table S3:** Bond distances ($d$, Å) of the IS, TS and FS for all the reaction pathways.

| | $d_{MoA\text{-}O}$ | $d_{MoA\text{-}C}$ | $d_{MoA\text{-}H}$ | $d_{C\text{-}O}$ | $d_{C\text{-}H}$ | $d_{O\text{-}H}$ |
|---|---|---|---|---|---|---|
| IS1 | 2.345, 2.022 | 2.439 | 1.972, 2.004 | 1.505 | | |
| TS1 | 2.214, 2.089 | 2.168 | 1.889, 1.894 | 1.954 | | |
| FS1 | 2.186, 2.151, 2.180 | 2.122 | 1.885, 1.928 | 5.358 | | |
| IS2 | 2.345, 2.022 | 2.439 | 1.972, 2.004 | | 2.942 | |
| TS2 | 2.215, 2.249 | 2.358 | 1.731 | | 1.694 | |
| FS2 | 2.020, 2.267 | 3.068 | 3.370 | | 1.108 | |
| IS3 | 2.345, 2.022 | 2.439 | 1.972, 2.004 | | | 2.472 |
| TS3 | 2.235, 2.357 | 2.252 | 1.904 | | | 1.288 |
| FS3 | 2.332, 2.310 | 2.253 | 2.864 | | | 0.981 |
| IS4 | 2.092, 2.302 | 2.277 | 1.887, 1.879 | 1.320 | | |
| TS4 | 1.807, 2.953 | 2.346 | 1.888, 1.918 | 1.908 | | |
| FS4 | 1.727, 2.344 | 2.125, 2.348 | 1.874, 1.935 | 4.440 | | |
| IS5 | 2.147, 2.181, 2.151 | 2.153 | 1.915, 1.896 | | 2.685 | |
| TS5 | 2.211, 2.164, 2.163 | 2.154 | 1.762 | | 1.658 | |
| FS5 | 2.015, 2.167, 2.166 | 2.375, 2.489 | | | 1.101 | |
| IS6 | 2.147, 2.182, 2.151 | 2.153 | 1.915, 1.896 | | | 3.050 |
| TS6 | 2.139, 2.149 | 2.161 | 1.978 | | | 1.426 |
| FS6 | 2.148, 2.343 | 2.146 | | | | 0.983 |
| IS7 | 2.002, 2.184, 2.156 | 2.428, 2.461 | 1.914, 1.897 | | 3.230 | |
| TS7 | 2.093, 2.168, 2.169 | 2.393 | 1.886, 1.958 | | 1.587 | |
| FS7 | 2.164, 2.156, 2.168, 2.169 | | | | 1.106 | |
| IS8 | 2.002, 2.184, 2.156 | 2.428, 2.461 | 1.914, 1.897 | | | 3.051 |
| TS8 | 2.008, 2.168 | 2.377, 2.502 | 1.849 | | | 1.398 |
| FS8 | 2.021, 2.358 | 2.345, 2.523 | | | | 0.979 |
| IS9 | 2.175, 2.148, 2.156, 2.188 | | 1.915, 1.933 | | | 3.078 |
| TS9 | 2.164, 2.156, 2.172 | | 1.949 | | | 1.411 |
| FS9 | 2.326, 2.171, 2.164 | | | | | 0.980 |
| IS10 | 2.144, 2.188, 2.184, 2.159 | | 1.919, 1.908 | | | 3.068 |
| TS10 | 2.153, 2.171, 2.148 | | 1.961 | | | 1.399 |
| FS10 | 2.165, 2.159, 2.346 | | | | | 0.979 |
| IS11 | 2.161,2.185,2.316 | | 1.880,1.930 | | | 3.055 |
| TS11 | 2.157,2.317 | | 1.949 | | | 1.355 |
| FS11 | 2.350,2.332 | | | | | 0.978 |
| IS12 | 2.334,2.154,2.170 | | 1.897,1.949 | | | 3.065 |
| TS12 | 2.339,2.178 | | 1.938 | | | 1.389 |
| FS12 | 2.350,2.332 | | | | | 0.980 |
| IS13 | 2.327 | | 1.900, 1.888 | 1.461 | | |
| TS13 | 2.097 | | 1.897, 1.863 | 2.160 | | |
| FS13 | 2.164, 2.164 | 2.231 | 1.838, 1.847 | 4.895 | | |
| IS14 | 2.150, 2.181 | 2.260 | 1.876, 1.913 | | 2.602 | |
| TS14 | 2.161, 2.173 | 2.411 | 1.759 | | 1.646 | |
| FS14 | 2.167, 2.170 | | 2.148 | | 1.101 | |
| IS15 | 2.150, 2.181 | 2.260 | 1.876, 1.913 | | | 3.015 |
| TS15 | 2.130 | 2.267 | 1.968 | | | 1.453 |

| | | | | | | |
|---|---|---|---|---|---|---|
| FS15 | 2.318 | 2.239 | | | | 0.983 |
| IS16 | 2.186, 2.151, 2.180 | 2.122 | 1.928, 1.885 | | | 2.702 |
| TS16 | 2.350, 2.165, 2.164 | 2.086 | 1.830 | | | 1.309 |
| FS16 | 2.401, 2.169, 2.169 | 2.039 | | | | 0.984 |
| IS17 | 2.147, 2.182, 2.151 | 2.153 | 1.915, 1.896 | 1.279 | | |
| TS17 | 1.807, 2.189, 2.153 | 1.920 | 1.899, 1.933 | 1.937 | | |
| FS17 | 1.925, 2.083, 2.163, 2.179 | 2.222, 2.088 | | 3.278 | | |
| IS18 | 2.035, 2.157, 2.181 | 2.418, 2.466 | 1.941, 1.827 | | | 2.342 |
| TS18 | 2.201, 2.164, 2.180 | 2.421, 2.510 | 1.851 | | | 1.339 |
| FS18 | 2.24, 2.178, 2.1693 | 2.286 | | | | 0.981 |
| IS19 | 2.002, 2.184, 2.156 | 2.428, 2.461 | 1.914, 1.897 | 1.369 | | |
| TS19 | 1.796, 2.185, 2.160 | 2.497, 2.067, 2.506 | 1.913, 1.894 | 2.080 | | |
| FS19 | 1.926, 2.090, 2.161, 2.229 | 2.168, 2.216, 2.497 | 1.915, 1.951, 1.938 | 3.071 | | |
| IS20 | 2.144, 2.188, 2.184, 2.159 | | 1.919, 1.908 | 1.431 | | |
| TS20 | 1.796, 2.175, 2.168 | 3.350 | 1.911, 1.860 | 2.066 | | |
| FS20 | 1.727, 2.169, 2.152 | 2.232 | 1.878, 1.857 | 3.223 | | |
| IS21 | 2.150, 2.181 | 2.260 | 1.876, 1.913 | | 1.144 | |
| TS21 | 2.153, 2.182 | 2.287 | 1.843, 1.919, 1.753 | | 1.780 | |
| FS21 | 2.183, 2.158 | 2.260, 2.467 | 1.992, 2.038, 2.021, 1.928, 1.885 | | 2.954 | |
| 2OH | 2.141, 2.190, 2.141, 2.190 | | | | | 3.305, 0.976 |
| TS(H-OH) | 2.088, 1.861 | | | | | 1.427, 1.077 |
| $H_2O$+O | 2.275, 1.760 | | | | | 1.013, 1.680 |

**Table S4:** Reaction barrier $E_a$ (eV) and reaction energy $E_r$ (eV) of all the reaction pathways (values including ZPE in parentheses, R represents the propyl group)

| *Reaction pathway* | $E_a$ | $E_r$ |
|---|---|---|
| R-COOH+H → TS1 → R-CO+OH+H | 0.25 (0.19) | -0.88 (-0.94) |
| R-COOH+H → TS2 → R-CHO(OH) | 1.29 (1.23) | -0.35 (-0.22) |
| R-COOH+H → TS3 →R-C(OH)$_2$ | 1.38 (1.31) | 0.77 (0.88) |
| R-COOH+H → TS4 →R-COH+O+H | 1.31 (1.24) | -0.02 (-0.07) |
| R-CO+OH+H → TS5 → R-CHO+OH | 0.83 (0.79) | -0.19 (-0.09) |
| R-CO + OH +H → TS6 → R-CO + $H_2O$ | 1.41 (1.30) | 0.61 (0.68) |
| R-CHO+OH+H → TS7 → R-$CH_2O$+OH | 0.95 (0.91) | -0.19 (-0.09) |
| R-CHO+OH+H → TS8 → R-CHO+$H_2O$ | 1.56 (1.47) | 0.48 (0.56) |
| R-$CH_2O$+OH+H → TS9 → R-$CH_2OH$+OH | 1.36 (1.26) | 0.29 (0.40) |
| R-$CH_2O$+OH+H → TS10 → R-$CH_2O$+$H_2O$ | 1.44 (1.36) | 0.50 (0.60) |
| R-$CH_2OH$+OH+H → TS11 → R-$CH_2OH$+$H_2O$ | 1.52 (1.44) | 0.69 (0.79) |
| R-$CH_2O$+$H_2O$ → TS12 → R-$CH_2OH$+$H_2O$ | 1.50 (1.41) | 0.57 (0.70) |
| R-$CH_2OH$+H → TS13 → R-$CH_2$+OH+H | 1.63 (1.50) | -0.75 (-0.83) |
| R-$CH_2$+OH+H → TS14 → R-$CH_3$+OH | 0.74 (0.70) | -0.46 (-0.35) |
| R-$CH_2$+OH+H → TS15 → R-$CH_2$+$H_2O$ | 1.31 (1.20) | 0.44 (0.52) |
| R-CO+OH+H → TS16 → R-COH+OH | 1.90 (1.79) | 1.08 (1.18) |
| R-CO+OH+H → TS17 → R-C+O+OH+H | 1.80 (1.70) | 0.16 (0.09) |
| R-CHO+OH+H → TS18 → R-CHOH+OH | 1.41 (1.34) | 0.45 (0.58) |
| R-CHO+OH+H → TS19 → R-CH+O+OH+H | 1.15 (1.10) | 0.41 (0.33) |
| R-$CH_2O$+OH+H → TS20 → R-$CH_2$+O+OH+H | 2.31 (2.19) | 0.17 (0.10) |
| R-$CH_2$+OH+H → TS21 → R'-CH=$CH_2$+2H+OH | 1.17 (1.00) | 0.12 (0.00) |
| 2OH → TS(H-OH) →$H_2O$ + O | 0.41 (0.33) | 0.23 (0.23) |

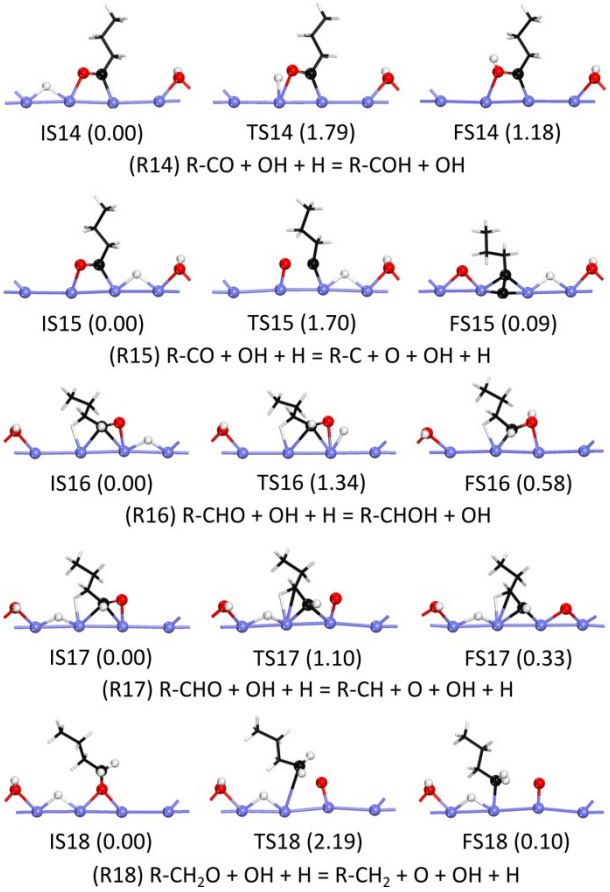


**Figure S1:** Side views of all the optimized geometries for the C-O dissociation and hydrogenation of O atom (Mo/blue, H/white, C/black, O/red)

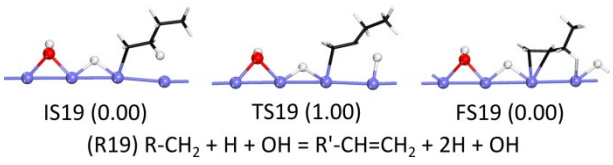


**Figure S2:** Side views of the optimized geometries for the β-H elimination of R-$CH_2$ (Mo/blue, H/white, C/black, O/red)

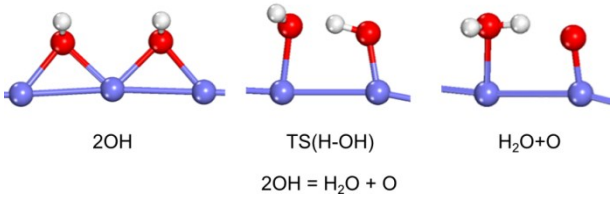


**Figure S3:** Side views of the optimized geometries for the disproportionation of OH (Mo/blue, H/white, O/red).