Table 1.1: Adsorption energies ($E_{ads}$, eV) of intermediates in the $CO_2$ reduction reaction towards $CH_4$ and methanol on Cu clusters. Hollow sites are maked as either hollow, FCC, or HCP.

| Absorbate | | Cu(111) | | $Cu_{55}$ | | $Cu_{147}$ | | $Cu_{78,1}$ | | $Cu_{78,2}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $E_{ads}$ | Site | $E_{ads}$ | Site | $E_{ads}$ | Site | $E_{ads}$ | Site | $E_{ads}$ | Site |
| (b) | COOH[a] | 0.76 | top-top | 0.49 | top-top | 0.47 | top-top | 0.38 | top-top | -0.03 | top-top |
| (c) | CO | 0.98 | top | 0.71 | top (corner) | 0.94 | top (corner) | 0.60 | hollow | 0.64/0.68[b] | bridge/bridge |
| (d) | CHO | 1.54 | top | 1.29 | top (C) | 1.37 | top (C) | 1.09 | bridge | 0.84 | top |
| (e) | COH | 2.12 | FCC | 2.02 | HCP | 2.33 | HCP | 1.78 | hollow | 1.89 | HCP |
| (f) | $CH_2O$ | 0.92 | DNB[c] | 0.90 | top (corner) | 1.07 | top (corner) | 0.71 | bridge-top | 0.78 | top |
| (g) | CHOH | 1.80 | bridge | 1.67 | bridge | 1.71 | bridge | 1.50 | bridge | 1.18 | bridge |
| (h) | $CH_3O$ | 0.06 | FCC | -0.05 | HCP | -0.16 | HCP | -0.44 | hollow | -0.52 | bridge |
| (i) | $CH_2OH$ | 1.06 | top | 0.82 | top (C) | 0.86 | top (C) | 0.64 | top | 0.35 | top |
| (j) | $CH_3$ | 0.16 | bridge | -0.05 | bridge | -0.14 | top (corner) | -0.36 | bridge | -0.53 | bridge |
| (k) | $CH_2$ | 1.11 | FCC | 0.92 | HCP | 1.01 | bridge | 0.66 | hollow | 0.63 | bridge |
| (l) | CH | 1.68 | FCC | 1.35 | dist. 4-fold | 1.74 | dist. 4-fold | 1.17 | 4-fold | 0.93/1.16[b] | 4-fold/4-fold |
| (m) | C | 3.05 | FCC | 2.49 | dist. 4-fold | 2.83 | dist. 4-fold | 2.08 | 4-fold | 1.91/2.26[b] | 4-fold/4-fold |
| (n) | OH | 0.03 | FCC | -0.12 | HCP | -0.19 | HCP | -0.51 | hollow | -0.68 | bridge |
| (o) | O | 0.72 | FCC | 0.54 | HCP | 0.52 | HCP | 0.17 | hollow | 0.38/0.50[b] | hollow/4-fold |

a: -0.45 added to energy to account for poor description of C=O bonds with DFT. b: Two adsorption energies are given. The first is the adsorption energy for the strongest binding site. This binding site was located on the other side of the cluster from where the *COOH moiety had initial adsorbed to. The second is the adsorption energy of a binding site near where the *COOH moiety had initially adsorbed to. c: Did not bind.