# Electronic Supporting Information

**Methanol oxidation on Ru(0001) for direct methanol fuel cells: Analysis of the competitive reaction mechanism**

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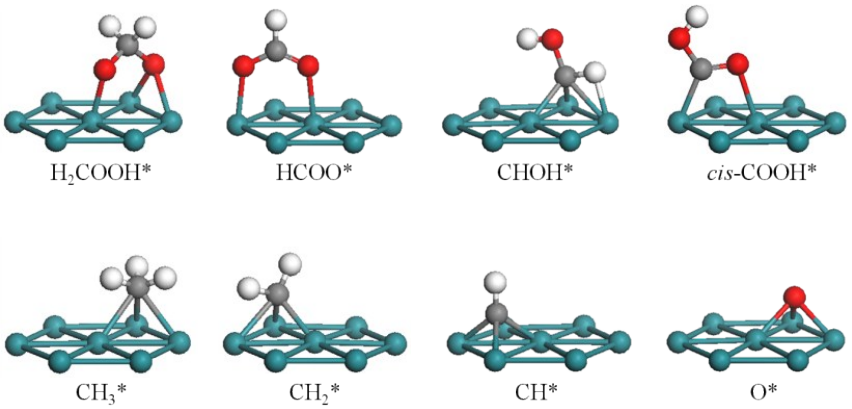


**Figure S1.** Intermediates involved in $CH_3OH$ oxidation on Ru (0001). Parameters follow the same notation as in Figure 1.

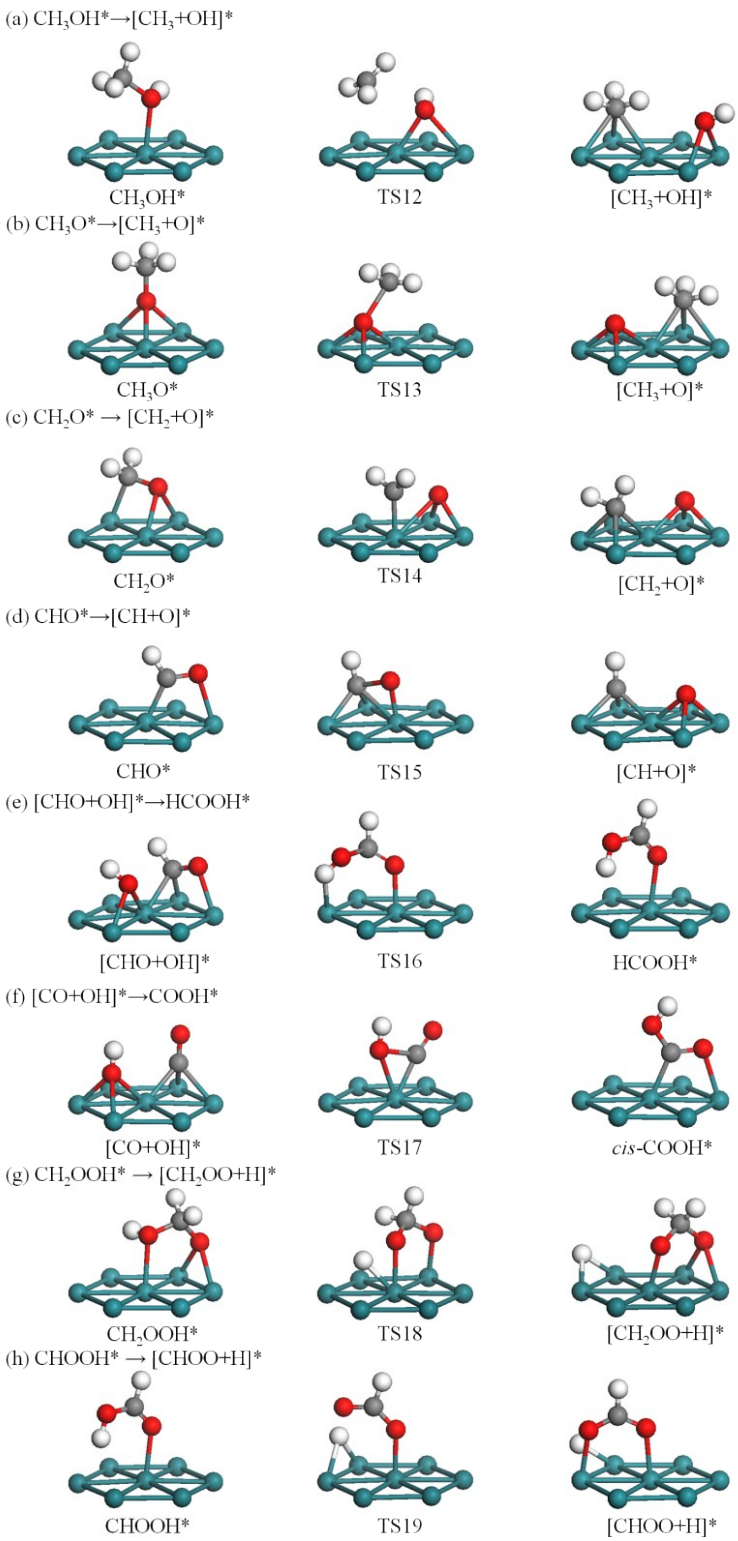


**Figure S2.** The C–O bond scissions of $CH_3OH$ (a), $CH_3O$ (b), $CH_2O$ (c) and CHO (d), the combination of CHO and OH to form HCOOH (e), the reaction of CO with OH to form *cis*-COOH (f), the dehydrogenation of $CH_2OOH$ to $CH_2OO$ (g) and further dehydrogenation to CHOO (h).

**Table S1.** Adsorption sites, adsorption energies (in eV), and structural parameters (in angstroms and degrees) for intermediates involved in $CH_3OH$ oxidation on Ru(0001).

| species | site | configuration | $E_{ads}$ | $d_{C/H–Ru}$ | $d_{O–Ru}$ | angles[a] |
|---|---|---|---|---|---|---|
| $H_2COO^*$ | hcp | $\eta^1$(O)-$\eta^2$(O) | 4.66 | | 2.02, 2.15, 2.18 | 72 |
| $HCOO^*$ | bridge | $\eta^1$(O) | 3.24 | | 2.15, 2.15 | 0 |
| $CHOH^*$ | fcc | $\eta^2$(C) | 3.36 | | 2.11, 2.11 | 26 |
| | hcp | $\eta^3$(O) | 3.42 | | 2.10, 2.10 | 43 |
| *cis*-$COOH^*$ | bridge | $\eta^1$(C)-$\eta^1$(O) | 2.68 | 2.05 | 2.21 | 31, 85 |
| | fcc | $\eta^1$(C) | 2.67 | 2.03 | | 29, 84 |
| | hcp | $\eta^1$(C) | 2.68 | 2.03 | | 30, 83 |
| $CH_3^*$ | fcc | $\eta^3$(C) | 2.23 | 2.22, 2.22, 2.22 | | |
| | hcp | $\eta^3$(C) | 2.19 | 2.20, 2.21, 2.20 | | |
| | top | $\eta^1$(C) | 1.86 | 2.15 | | |
| $CH_2^*$ | fcc | $\eta^3$(C) | 5.00 | 2.09, 2.09, 2.24 | | |
| | hcp | $\eta^3$(C) | 5.07 | 2.09, 2.09, 2.20 | | |
| $CH^*$ | fcc | $\eta^3$(C) | 6.42 | 2.03, 2.03, 2.03 | | |
| | hcp | $\eta^3$(C) | 6.63 | 2.02, 2.02, 2.02 | | |
| | top | $\eta^1$(C) | 5.19 | 1.73 | | |
| $O^*$ | fcc | $\eta^3$(O) | 5.45 | | 2.05, 2.05, 2.05 | |
| | hcp | $\eta^3$(O) | 5.71 | | 2.02, 2.02, 2.02 | |

[a] Values are angles between the surface normal and the C−O axis in the corresponding species.