**Supporting Information**

# Automated Generation and Analysis of the Complex Catalytic Reaction Network of Ethanol Synthesis from Syngas on Rh(111)

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**Species and elementary steps generated for the reaction network of syngas to ethanol**

**1. Species generated for Network-initial**

**Gas:**

CO, $H_2$, $H_2O$, $CH_3CH_2OH$

**Intermediates:**

H*, OH*, O*, CO*, $CH_3OH$*, C*, CH*, $CH_2$*, $CH_3$*, CHO*, COH*, $CH_2O$*, CHOH*, $CH_3O$*, $CH_2OH$*, CCO*, CHCO*, CCHO*, CCOH*, CHCHO*, $CCH_2O$*, CCHOH*, CHCOH*, $CH_2CO$*, $CHCH_2O$*, $CCH_2OH$*, CHCHOH*, $CH_3CO$*, $CH_2CHO$*, $CH_2COH$*, $CHCH_2OH$*, $CH_3CHO$*, $CH_2CH_2O$*, $CH_2CHOH$*, $CH_3COH$*, $CH_3CH_2O$*, $CH_2CH_2OH$*, $CH_3CHOH$*, HCOO*, COOH*, HCOOH*, $CH_2OO$*, $CH_2OOH$*,

**Transition States:**

O-H*, H-OH*, C-H*, CH-H*, $CH_2$-H*, H-CO*, CO-H*, H-CHO*, CHO-H*, H-$CH_2O$*, $CH_2O$-H*, H-COOH*, H-CHOO*, $CH_2OO$-H*, H-CCO*, CC(-H)O*, CCO-H*, H-CCHO*, CCH(-H)O*, CCHO-H*, H-CCOH*, H-CHCO*, H-$CCH_2O$*, $CCH_2O$-H*, H-CCHOH*, H-$CH_2CO$*, $CH_2C$(-H)O*, $CH_2CO$-H*, H-$CCH_2OH$*, H-$CH_2CHO$*, $CH_2CH$(-H)O*, $CH_2CHO$-H*, H-$CH_2COH$*, H-$CH_2CH_2O$*, $CH_2CH_2O$-H*, H-$CH_2CHOH$*, H-CHCOH*, CHC(-H)OH*, $CH_3O$-H*, CHC(-H)O*, CHCO-H*, H-COH*, HCOO-H*, $CH_2C$(-H)OH*, $CH_3C$(-H)O*, $CH_3CO$-H*, CH(-H)$CH_2O$*, $CHCH_2O$-H*, H-CHCHOH*, CHCH(-H)OH*, H-CHOH*, CCH(-H)OH*, H-CHOOH*, $CH_2CH$(-H)OH*, $CH_3CH$(-H)O*, $CH_3CHO$-H*, $CH_3C$(-H)OH*, CH(-H)$CH_2OH$*, H-$CH_2CH_2OH$*, $CH_3CH_2O$-H*, $CH_3CH$(-H)OH*, H-$CH_2OH$*, CC(-H)OH*, H-CHCHO*, CHCH(-H)O*, CHCHO-H*, C-O*, CH-O*, $CH_2$-O*, $CH_3$-O*, CHO-O*, O-$CH_2O$*, O-COH*, O-CHOH*, O-$CH_2OH$*, C-OH*, CH-OH*, $CH_2$-OH*, $CH_3$-OH*, CO-OH*, HCO-OH*, $CH_2O$-OH*, C-CO*, C-CHO*, C-COH*, C-$CH_2O$*, C-CHOH*, C-$CH_2OH$*, CH-CO*, CH-CHO*, CH-COH*, CH-$CH_2O$*, CH-CHOH*, CH-$CH_2OH$*, $CH_2$-CO*, $CH_2$-CHO*, $CH_2$-COH*, $CH_2$-$CH_2O$*, $CH_2$-CHOH*, $CH_2$-

$CH_2OH^*$, $CH_3$-CO*, $CH_3$-CHO*, $CH_3$-COH*, $CH_3$-$CH_2O^*$, $CH_3$-CHOH*, $CH_3$-$CH_2OH^*$

**2. Elementary steps generated for Reaction Network**

The elementary steps generated for syngas to ethanol reaction are divided into three parts.

Network-initial is Part one + Part two + Part three

Network-ref is Part one + Part two + Part four

Network-final is Part one

**Part One**

| | | | | | |
|---|---|---|---|---|---|
| R1: | $H_2(g)$ + 2* | ↔ | 2H* | | |
| R2: | CO(g)+ * | ↔ | CO* | | |
| R3: | H* + O* | ↔ | O-H* | + * ↔ OH* | + * |
| R4: | H* + OH* | ↔ | H-OH* | + * ↔ $H_2O(g)$ | + 2* |
| R5: | H* + C* | ↔ | C-H* | + * ↔ CH* | + * |
| R6: | H* + CH* | ↔ | CH-H* | + * ↔ $CH_2$* | + * |
| R7: | H* + $CH_2$* | ↔ | CH2-H* | + * ↔ $CH_3$* | + * |
| R8: | H* + CO* | ↔ | H-CO* | + * ↔ CHO* | + * |
| R9: | H* + CO* | ↔ | CO-H* | + * ↔ COH* | + * |
| R10: | H* + CHO* | ↔ | H-CHO* | + * ↔ $CH_2O$* | + * |
| R11: | H* + CHO* | ↔ | CHO-H* | + * ↔ CHOH* | + * |
| R12: | H* + $CH_2O$* | ↔ | H-$CH_2O$* | + * ↔ $CH_3O$* | + * |
| R13: | H* + $CH_2O$* | ↔ | $CH_2O$-H* | + * ↔ $CH_2OH$* | + * |
| R14: | H* + CCO* | ↔ | H-CCO* | + * ↔ CHCO* | + * |
| R15: | H* + CCO* | ↔ | CC(-H)O* | + * ↔ CCHO* | + * |
| R16: | H* + CCO* | ↔ | CCO-H* | + * ↔ CCOH* | + * |
| R17: | H* + CCHO* | ↔ | H-CCHO* | + * ↔ CHCHO* | + * |
| R18: | H* + CCHO* | ↔ | CCH(-H)O* | + * ↔ $CCH_2O$* | + * |
| R19: | H* + CCHO* | ↔ | CCHO-H* | + * ↔ CCHOH* | + * |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| R20: | H* | + CCOH* | ↔ | H-CCOH* | + * ↔ | CHCOH* | + * |
| R21: | H* | + CHCO* | ↔ | H-CHCO* | + * ↔ | $CH_2CO$* | + * |
| R22: | H* | + $CCH_2O$* | ↔ | H-$CCH_2O$* | + * ↔ | $CHCH_2O$* | + * |
| R23: | H* | + $CCH_2O$* | ↔ | $CCH_2O$-H* | + * ↔ | $CCH_2OH$* | + * |
| R24: | H* | + CCHOH* | ↔ | H-CCHOH* | + * ↔ | CHCHOH* | + * |
| R25: | H* | + $CH_2CO$* | ↔ | H-$CH_2CO$* | + * ↔ | $CH_3CO$* | + * |
| R26: | H* | + $CH_2CO$* | ↔ | $CH_2C$(-H)O* | + * ↔ | $CH_2CHO$* | + * |
| R27: | H* | + $CH_2CO$* | ↔ | $CH_2CO$-H* | + * ↔ | $CH_2COH$* | + * |
| R28: | H* | + $CCH_2OH$* | ↔ | H-$CCH_2OH$* | + * ↔ | $CHCH_2OH$* | + * |
| R29: | H* | + $CH_2CHO$* | ↔ | H-$CH_2CHO$* | + * ↔ | $CH_3CHO$* | + * |
| R30: | H* | + $CH_2CHO$* | ↔ | $CH_2CH$(-H)O* | + * ↔ | $CH_2CH_2O$* | + * |
| R31: | H* | + $CH_2CHO$* | ↔ | $CH_2CHO$-H* | + * ↔ | $CH_2CHOH$* | + * |
| R32: | H* | + $CH_2COH$* | ↔ | H-$CH_2COH$* | + * ↔ | $CH_3COH$* | + * |
| R33: | H* | + $CH_2CH_2O$* | ↔ | H-$CH_2CH_2O$* | + * ↔ | $CH_3CH_2O$* | + * |
| R34: | H* | + $CH_2CH_2O$* | ↔ | $CH_2CH_2O$-H* | + * ↔ | $CH_2CH_2OH$* | + * |
| R35: | H* | + $CH_2CHOH$* | ↔ | H-$CH_2CHOH$* | + * ↔ | $CH_3CHOH$* | + * |
| R36: | H* | + CHCOH* | ↔ | H-CHCOH* | + * ↔ | $CH_2COH$* | + * |
| R37: | H* | + CHCOH* | ↔ | CHC(-H)OH* | + * ↔ | CHCHOH* | + * |
| R38: | H* | + $CH_3O$* | ↔ | $CH_3O$-H* | + * ↔ | $CH_3OH$* | + * |
| R39: | H* | + CHCO* | ↔ | CHC(-H)O* | + * ↔ | CHCHO* | + * |
| R40: | H* | + CHCO* | ↔ | CHCO-H* | + * ↔ | CHCOH* | + * |
| R41: | H* | + COH* | ↔ | H-COH* | + * ↔ | CHOH* | + * |
| R42: | H* | + $CH_2COH$* | ↔ | $CH_2C$(-H)OH* | + * ↔ | $CH_2CHOH$* | + * |
| R43: | H* | + $CH_3CO$* | ↔ | $CH_3C$(-H)O* | + * ↔ | $CH_3CHO$* | + * |
| R44: | H* | + $CH_3CO$* | ↔ | $CH_3CO$-H* | + * ↔ | $CH_3COH$* | + * |
| R45: | H* | + $CHCH_2O$* | ↔ | CH(-H)$CH_2O$* | + * ↔ | $CH_2CH_2O$* | + * |
| R46: | H* | + $CHCH_2O$* | ↔ | $CHCH_2O$-H* | + * ↔ | $CHCH_2OH$* | + * |
| R47: | H* | + CHCHOH* | ↔ | H-CHCHOH* | + * ↔ | $CH_2CHOH$* | + * |
| R48: | H* | + CHCHOH* | ↔ | CHCH(-H)OH* | + * ↔ | $CHCH_2OH$* | + * |
| R49: | H* | + CHOH* | ↔ | H-CHOH* | + * ↔ | $CH_2OH$* | + * |

R50: $H^* + CCHOH^* \leftrightarrow CCH(-H)OH^* + * \leftrightarrow CCH_2OH^* + *$

R51: $H^* + CH_2CHOH^* \leftrightarrow CH_2CH(-H)OH^* + * \leftrightarrow CH_2CH_2OH^* + *$

R52: $H^* + CH_3CHO^* \leftrightarrow CH_3CH(-H)O^* + * \leftrightarrow CH_3CH_2O^* + *$

R53: $H^* + CH_3CHO^* \leftrightarrow CH_3CHO\text{-}H^* + * \leftrightarrow CH_3CHOH^* + *$

R54: $H^* + CH_3COH^* \leftrightarrow CH_3C(-H)OH^* + * \leftrightarrow CH_3CHOH^* + *$

R55: $H^* + CHCH_2OH^* \leftrightarrow CH(-H)CH_2OH^* + * \leftrightarrow CH_2CH_2OH^* + *$

R56: $H^* + CH_2CH_2OH^* \leftrightarrow H\text{-}CH_2CH_2OH^* + * \leftrightarrow CH_3CH_2OH(g) + 2*$

R57: $H^* + CH_3CH_2O^* \leftrightarrow CH_3CH_2O\text{-}H^* + * \leftrightarrow CH_3CH_2OH(g) + 2*$

R58: $H^* + CH_3CHOH^* \leftrightarrow CH_3CH(-H)OH^* + * \leftrightarrow CH_3CH_2OH(g) + 2*$

R59: $H^* + CH_2OH^* \leftrightarrow H\text{-}CH_2OH^* + * \leftrightarrow CH_3OH^* + *$

R60: $H^* + CCOH^* \leftrightarrow CC(-H)OH^* + * \leftrightarrow CCHOH^* + *$

R61: $H^* + CHCHO^* \leftrightarrow H\text{-}CHCHO^* + * \leftrightarrow CH_2CHO^* + *$

R62: $H^* + CHCHO^* \leftrightarrow CHCH(-H)O^* + * \leftrightarrow CHCH_2O^* + *$

R63: $H^* + CHCHO^* \leftrightarrow CHCHO\text{-}H^* + * \leftrightarrow CHCHOH^* + *$

R64: $O^* + C^* \leftrightarrow C\text{-}O^* + * \leftrightarrow CO^* + *$

R65: $O^* + CH^* \leftrightarrow CH\text{-}O^* + * \leftrightarrow CHO^* + *$

R66: $O^* + CH_2^* \leftrightarrow CH_2\text{-}O^* + * \leftrightarrow CH_2O^* + *$

R67: $O^* + CH_3^* \leftrightarrow CH_3\text{-}O^* + * \leftrightarrow CH_3O^* + *$

R68: $OH^* + C^* \leftrightarrow C\text{-}OH^* + * \leftrightarrow COH^* + *$

R69: $OH^* + CH^* \leftrightarrow CH\text{-}OH^* + * \leftrightarrow CHOH^* + *$

R70: $OH^* + CH_2^* \leftrightarrow CH_2\text{-}OH^* + * \leftrightarrow CH_2OH^* + *$

R71: $OH^* + CH_3^* \leftrightarrow CH_3\text{-}OH^* + * \leftrightarrow CH_3OH^* + *$

R72: $C^* + CO^* \leftrightarrow C\text{-}CO^* + * \leftrightarrow CCO^* + *$

R73: $C^* + CHO^* \leftrightarrow C\text{-}CHO^* + * \leftrightarrow CCHO^* + *$

R74: $C^* + COH^* \leftrightarrow C\text{-}COH^* + * \leftrightarrow CCOH^* + *$

R75: $C^* + CH_2O^* \leftrightarrow C\text{-}CH_2O^* + * \leftrightarrow CCH_2O^* + *$

R76: $C^* + CHOH^* \leftrightarrow C\text{-}CHOH^* + * \leftrightarrow CCHOH^* + *$

R77: $C^* + CH_2OH^* \leftrightarrow C\text{-}CH_2OH^* + * \leftrightarrow CCH_2OH^* + *$

R78: $CH^* + CO^* \leftrightarrow CH\text{-}CO^* + * \leftrightarrow CHCO^* + *$

R79: $CH^* + CHO^* \leftrightarrow CH\text{-}CHO^* + * \leftrightarrow CHCHO^* + *$

R80: $CH^* + COH^* \leftrightarrow CH\text{-}COH^* + * \leftrightarrow CHCOH^* + *$

R81: $CH^* + CH_2O^* \leftrightarrow CH\text{-}CH_2O^* + * \leftrightarrow CHCH_2O^* + *$

R82: $CH^* + CHOH^* \leftrightarrow CH\text{-}CHOH^* + * \leftrightarrow CHCHOH^* + *$

R83: $CH^* + CH_2OH^* \leftrightarrow CH\text{-}CH_2OH^* + * \leftrightarrow CHCH_2OH^* + *$

R84: $CH_2^* + CO^* \leftrightarrow CH_2\text{-}CO^* + * \leftrightarrow CH_2CO^* + *$

R85: $CH_2^* + CHO^* \leftrightarrow CH_2\text{-}CHO^* + * \leftrightarrow CH_2CHO^* + *$

R86: $CH_2^* + COH^* \leftrightarrow CH_2\text{-}COH^* + * \leftrightarrow CH_2COH^* + *$

R87: $CH_2^* + CH_2O^* \leftrightarrow CH_2\text{-}CH_2O^* + * \leftrightarrow CH_2CH_2O^* + *$

R88: $CH_2^* + CHOH^* \leftrightarrow CH_2\text{-}CHOH^* + * \leftrightarrow CH_2CHOH^* + *$

R89: $CH_2^* + CH_2OH^* \leftrightarrow CH_2\text{-}CH_2OH^* + * \leftrightarrow CH_2CH_2OH^* + *$

R90: $CH_3^* + CO^* \leftrightarrow CH_3\text{-}CO^* + * \leftrightarrow CH_3CO^* + *$

R91: $CH_3^* + CHO^* \leftrightarrow CH_3\text{-}CHO^* + * \leftrightarrow CH_3CHO^* + *$

R92: $CH_3^* + COH^* \leftrightarrow CH_3\text{-}COH^* + * \leftrightarrow CH_3COH^* + *$

R93: $CH_3^* + CH_2O^* \leftrightarrow CH_3\text{-}CH_2O^* + * \leftrightarrow CH_3CH_2O^* + *$

R94: $CH_3^* + CHOH^* \leftrightarrow CH_3\text{-}CHOH^* + * \leftrightarrow CH_3CHOH^* + *$

R95: $CH_3^* + CH_2OH^* \leftrightarrow CH_3\text{-}CH_2OH^* + * \leftrightarrow CH_3CH_2OH(g) + 2*$

**Part Two**

R96: $H^* + COOH^* \leftrightarrow H\text{-}COOH^* + * \leftrightarrow HCOOH^* + *$

R97: $H^* + HCOO^* \leftrightarrow H\text{-}CHOO^* + * \leftrightarrow CH2OO^* + *$

R98: $H^* + CH_2OO^* \leftrightarrow CH_2OO\text{-}H^* + * \leftrightarrow CH_2OOH^* + *$

R99: $H^* + HCOO^* \leftrightarrow HCOO\text{-}H^* + * \leftrightarrow HCOOH^* + *$

R100: $H^* + HCOOH^* \leftrightarrow H\text{-}CHOOH^* + * \leftrightarrow CH_2OOH^* + *$

R101: $OH^* + CO^* \leftrightarrow CO\text{-}OH^* + * \leftrightarrow COOH^* + *$

R102: $O^* + CHO^* \leftrightarrow CHO\text{-}O^* + * \leftrightarrow HCOO^* + *$

R103: $O^* + CH_2O^* \leftrightarrow O\text{-}CH_2O^* + * \leftrightarrow CH_2OO^* + *$

R104: $OH^* + CHO^* \leftrightarrow HCO\text{-}OH^* + * \leftrightarrow HCOOH^* + *$

R105: $OH^* + CH_2O^* \leftrightarrow CH_2O\text{-}OH^* + * \leftrightarrow CH_2OOH^* + *$

**Part three**

R106:O* + COH* ↔ O-COH* + * ↔ COOH* + *

R107:O* + CHOH* ↔ O-CHOH* + * ↔ HCOOH* + *

R108:O* + $CH_2OH$* ↔ O-$CH_2OH$* + * ↔ $CH_2OOH$* + *

**Part four**

R109:H* + COOH* ↔ H-OCOH* + * ↔ HOCOH* + *

R110:OH* + COH* ↔ HO-COH* + * ↔ HOCOH* + *

R111:H* + CCOO* ↔ H-CCOO* + * ↔ CHCOO* + *

R112:H* + CCOO* ↔ CCOO-H* + * ↔ CCOOH* + *

R113:H* + CCOOH* ↔ H-CCOOH* + * ↔ CHCOOH* + *

R114:H* + CCOOH* ↔ CC(-H)OOH* + * ↔ CCHOOH* + *

R115:H* + CHCOO* ↔ H-CHCOO* + * ↔ $CH_2COO$* + *

R116:H* + OCCHO* ↔ H-OCCHO* + * ↔ HOCCHO* + *

R117:H* + OCCHO* ↔ OC(-H)CHO* + * ↔ OCHCHO* + *

R118:H* + OCCHO* ↔ COCH(-H)O* + * ↔ $COCH_2O$* + *

R119:H* + OCCHO* ↔ OCCHO-H* + * ↔ OCCHOH* + *

R120:H* + OCCOH* ↔ H-OCCOH* + * ↔ HOCCOH* + *

R121:H* + OCCOH* ↔ OC(-H)COH* + * ↔ HOCCHO* + *

R122:H* + OCCOH* ↔ OCC(-H)OH* + * ↔ OCCHOH* + *

R123:H* + CCHOOH* ↔ H-CCHOOH* + * ↔ CHCHOOH* + *

R124:H* + $CH_2COO$* ↔ H-$CH_2COO$* + * ↔ $CH_3COO$* + *

R125:H* + $CH_2COO$* ↔ $CH_2COO$-H* + * ↔ $CH_2COOH$* + *

R126:H* +$COCH_2O$* ↔ H-$OCCH_2O$* + * ↔ $HOCCH_2O$* + *

R127:H* + $COCH_2O$* ↔ $OCCH_2O$-H* + * ↔ $OCCH_2OH$* + *

R128:H* + HOCCHO* ↔ HOCCHO-H* + * ↔ HOCCHOH* + *

R129:H* + OCCHOH* ↔ OC(-H)CHOH* + * ↔ OCHCHOH* + *

R130:H* + OCHCHO* ↔ OCH(-H)CHO* + * ↔ $OCH_2CHO$* + *

R131:H* + $CH_2CHOO$* ↔ $CH_2$(-H)CHOO* + * ↔ $CH_3CHOO$* + *

R132:H* + $CH_2CHOO$* ↔ $CH_2CHOO$-H* + * ↔ $CH_2CHOOH$* + *

R133:H* + $CH_2COOH$* ↔ H-$CH_2COOH$* + * ↔ $CH_3COOH$* + *

R134: H* + $HOCCH_2O$* ↔ $HOCCH_2O$-H* + * ↔ $HOCCH_2OH$* + *

R135: H* + HOCCHOH* ↔ HOC(-H)CHOH* + * ↔ HOCHCHOH*+ *

R136: H* + $OCCH_2OH$* ↔ OC(-H)$CH_2OH$* + * ↔ $OCHCH_2OH$* + *

R137: H* + $OCH_2CHO$* ↔ $OCH_2CH$(-H)O* + * ↔ $OCH_2CH_2O$* + *

R138: H* + $OCH_2CHO$* ↔ $OCH_2CHO$-H* + * ↔ $OCH_2CHOH$* + *

R139: H* + $CH_2CHOOH$* ↔ H-$CH_2CHOOH$* + * ↔ $CH_3CHOOH$* + *

R140: H* + HOCHCHOH* ↔ HOCH(-H)CHOH* + * ↔ $HOCH_2CHOH$* + *

R141: H* + $OCH_2CH_2O$* ↔ $OCH_2CH_2O$-H* + * ↔ $OCH_2CH_2OH$*+ *

R142: H* + $HOCH_2CHOH$* ↔ $HOCH_2CH$(-H)OH* + * ↔ $HOCH_2CH_2OH$* + *

R143: H* + CHCOOH* ↔ H-CHCOOH* + * ↔ $CH_2COOH$* + *

R144: H* + CHCOOH* ↔ CHC(-H)OOH* + * ↔ CHCHOOH* + *

R145: H* + HOCCHO* ↔ HOCCH(-H)O* + * ↔ $HOCCH_2O$* + *

R146: H* + HOCCOH* ↔ HOCC(-H)OH* + * ↔ HOCCHOH* + *

R147: H* + $COCH_2O$* ↔ $OCCH_2O$-H* + * ↔ $OCCH_2OH$* + *

R148: H* + OCCHOH* ↔ H-OCCHOH* + * ↔ HOCCHOH* + *

R149: H* + OCCHOH* ↔ OCCH(-H)OH* + * ↔ $OCCH_2OH$* + *

R150: H* + OCHCHO* ↔ OCHCHO-H* + * ↔ OCHCHOH* + *

R151: H* + HOCCHO* ↔ OCHC(-H)OH* + * ↔ OCHCHOH* + *

R152: H* + $CH_2COOH$* ↔ $CH_2C$(-H)OOH* + * ↔ $CH_2CHOOH$* + *

R153: H* + $CH_3COO$* ↔ $CH_3C$(-H)OO* + * ↔ $CH_3CHOO$* + *

R154: H* + $CH_3COO$* ↔ $CH_3COO$-H* + * ↔ $CH_3COOH$* + *

R155: H* + CHCHOOH* ↔ CH(-H)CHOOH* + * ↔ $CH_2CHOOH$* + *

R156: H* + HOCCHOH* ↔ HOCCH(-H)OH* + * ↔ $HOCCH_2OH$* + *

R157: H* + $OCCH_2OH$* ↔ H-$OCCH_2OH$* + * ↔ $HOCCH_2OH$* + *

R158: H* + OCHCHOH* ↔ H-OCHCHOH* + * ↔ HOCHCHOH*+ *

R159: H* + OCHCHOH* ↔ OCH(-H)CHOH* + * ↔ $OCH_2CHOH$* + *

R160: H* + OCHCHOH* ↔ OCHCH(-H)OH* + * ↔ $OCHCH_2OH$* + *

R161: H* + $CH_3CHOO$* ↔ $CH_3CHOO$-H* + * ↔ $CH_3CHOOH$* + *

R162: H* + $CH_3COOH$* ↔ $CH_3C$(-H)OOH* + * ↔ $CH_3CHOOH$* + *

R163: H* + $OCH_2CHOH$* ↔ H-$OCH_2CHOH$* + * ↔ $HOCH_2CHOH$*+ *

R164:H* + $OCH_2CHOH$* ↔ $OCH_2CH(-H)OH$* + * ↔ $OCH_2CH_2OH$*+ *

R165:H* + $OCHCH_2OH$* ↔ $OCH(-H)CH_2OH$* + * ↔ $OCH_2CH_2OH$*+ *

R166:H* + $OCH_2CH_2OH$* ↔ H-$OCH_2CH_2OH$* + * ↔ $HOCH_2CH_2OH$*+ *

R167:H* + CHCOO* ↔ CHCOO-H* + * ↔ CHCOOH* + *

R168:O* + CCO* ↔ CCO-O* + * ↔ CCOO* + *

R169:O* + CCOH* ↔ O-CCOH* + * ↔ OCCOH* + *

R170:O* + CHCO* ↔ CHCO-O* + * ↔ CHCOO* + *

R171:O* + CHCO* ↔ O-CHCO* + * ↔ OCHCO* + *

R172:O* + CCHO* ↔ O-CCHO* + * ↔ OCCHO* + *

R173:O* + $CCH_2O$* ↔ O-$CCH_2O$* + * ↔ $COCH_2O$* + *

R174:O* + CCHOH* ↔ O-CCHOH* + * ↔ OCCHOH* + *

R175:O* + $CH_2CO$* ↔ $CH_2CO$-O* + * ↔ $CH_2COO$* + *

R176:O* + $CH_2CO$* ↔ O-$CH_2CO$* + * ↔ $COCH_2O$* + *

R177:O* + CHCHO* ↔ O-CHCHO* + * ↔ OCHCHO* + *

R178:O* + CHCOH* ↔ O-CHCOH* + * ↔ HOCCHO* + *

R179:O* + $CCH_2OH$* ↔ O-$CCH_2OH$* + * ↔ $OCCH_2OH$* + *

R180:O* + $CH_2CHO$* ↔ O-$CH_2CHO$* + * ↔ $OCH_2CHO$* + *

R181:O* + $CH_2CHO$* ↔ $CH_2CHO$-O* + * ↔ $CH_2CHOO$* + *

R182:O* + $CH_2COH$* ↔ $HOCCH_2$-O* + * ↔ $HOCCH_2O$* + *

R183:O* + $CH_3CO$* ↔ $CH_3CO$-O* + * ↔ $CH_3COO$* + *

R184:O* + $CHCH_2O$* ↔ O-$CHCH_2O$* + * ↔ $OCH_2CHO$* + *

R185:O* + CHCHOH* ↔ O-CHCHOH* + * ↔ OCHCHOH* + *

R186:O* + $CH_2CH_2O$* ↔ O-$CH_2CH_2O$* + * ↔ $OCH_2CH_2O$* + *

R187:O* + $CH_2CHOH$* ↔ O-$CH_2CHOH$* + * ↔ $OCH_2CHOH$* + *

R188:O* + $CH_3CHO$* ↔ $CH_3CHO$-O* + * ↔ $CH_3CHOO$* + *

R189:O* + $CHCH_2OH$* ↔ O-$CHCH_2OH$* + * ↔ $OCHCH_2OH$* + *

R190:O* + $CH_2CH_2OH$* ↔ O-$CH_2CH_2OH$* + * ↔ $OCH_2CH_2OH$*+ *

R191:OH* + CCO* ↔ CCO-OH* + * ↔ CCOOH* + *

R192:OH* + CCO* ↔ OCC-OH* + * ↔ OCCOH* + *

R193:OH* + CCHO* ↔ HO-CCHO* + * ↔ HOCCHO* + *

R194: $OH^* + CCHO^* \leftrightarrow CCHO\text{-}OH^* + * \leftrightarrow CCHOOH^* + *$

R195: $OH^* + CCHO^* \leftrightarrow OCHC\text{-}OH^* + * \leftrightarrow HOCCHO^* + *$

R196: $OH^* + CCOH^* \leftrightarrow HO\text{-}CCOH^* + * \leftrightarrow HOCCOH^* + *$

R197: $OH^* + CHCO^* \leftrightarrow CHCO\text{-}OH^* + * \leftrightarrow CHCOOH^* + *$

R198: $OH^* + CHCO^* \leftrightarrow OCCH\text{-}OH^* + * \leftrightarrow OCCHOH^* + *$

R199: $OH^* + CCH_2O^* \leftrightarrow HO\text{-}CCH_2O^* + * \leftrightarrow HOCCH_2O^* + *$

R200: $OH^* + CCHOH^* \leftrightarrow HO\text{-}CCHOH^* + * \leftrightarrow HOCCHOH^* + *$

R201: $OH^* + CH_2CO^* \leftrightarrow CH_2CO\text{-}OH^* + * \leftrightarrow CH_2COOH^* + *$

R202: $OH^* + CH_2CO^* \leftrightarrow OCCH_2\text{-}OH^* + * \leftrightarrow OCCH_2OH^* + *$

R203: $OH^* + CHCHO^* \leftrightarrow CHCHO\text{-}OH^* + * \leftrightarrow CHCHOOH^* + *$

R204: $OH^* + CHCHO^* \leftrightarrow OCHCH\text{-}OH^* + * \leftrightarrow OCHCHOH^* + *$

R205: $OH^* + CHCOH^* \leftrightarrow HOCCH\text{-}OH^* + * \leftrightarrow HOCCHOH^* + *$

R206: $OH^* + CCH_2OH^* \leftrightarrow HO\text{-}CCH_2OH^* + * \leftrightarrow HOCCH_2OH^* + *$

R207: $OH^* + CH_2CHO^* \leftrightarrow CH_2CHO\text{-}OH^* + * \leftrightarrow CH_2CHOOH^* + *$

R208: $OH^* + CH_2CHO^* \leftrightarrow OCHCH_2\text{-}OH^* + * \leftrightarrow OCHCH_2OH^* + *$

R209: $OH^* + CH_2COH^* \leftrightarrow HOCCH_2\text{-}OH^* + * \leftrightarrow HOCCH_2OH^* + *$

R210: $OH^* + CH_3CO^* \leftrightarrow CH_3CO\text{-}OH^* + * \leftrightarrow CH_3COOH^* + *$

R211: $OH^* + CHCH_2O^* \leftrightarrow OCH_2CH\text{-}OH^* + * \leftrightarrow OCH_2CHOH^* + *$

R212: $OH^* + CHCHOH^* \leftrightarrow HOCHCH\text{-}OH^* + * \leftrightarrow HOCHCHOH^* + *$

R213: $OH^* + CH_2CH_2O^* \leftrightarrow OCH_2CH_2\text{-}OH^* + * \leftrightarrow OCH_2CH_2OH^* + *$

R214: $OH^* + CH_2CHOH^* \leftrightarrow HO\text{-}CH_2CHOH^* + * \leftrightarrow HOCH_2CHOH^* + *$

R215: $OH^* + CH_3CHO^* \leftrightarrow CH_3CHO\text{-}OH^* + * \leftrightarrow CH_3CHOOH^* + *$

R216: $OH^* + CHCH_2OH^* \leftrightarrow HO\text{-}CHCH_2OH^* + * \leftrightarrow HOCH_2CHOH^* + *$

R217: $OH^* + CH_2CH_2OH^* \leftrightarrow HOCH_2CH_2\text{-}OH^* + * \leftrightarrow HOCH_2CH_2OH^* + *$

R218: $C^* + COOH^* \leftrightarrow C\text{-}COOH^* + * \leftrightarrow CCOOH^* + *$

R219: $C^* + HCOOH^* \leftrightarrow C\text{-}CHOOH^* + * \leftrightarrow CCHOOH^* + *$

R220: $CH^* + COOH^* \leftrightarrow CH\text{-}COOH^* + * \leftrightarrow CHCOOH^* + *$

R221: $CH^* + HCOOH^* \leftrightarrow CH\text{-}CHOOH^* + * \leftrightarrow CHCHOOH^* + *$

R222: $CH_2^* + COOH^* \leftrightarrow CH_2\text{-}COOH^* + * \leftrightarrow CH_2COOH^* + *$

R223: $CH_2^* + HCOO^* \leftrightarrow CH_2\text{-}CHOO^* + * \leftrightarrow CH_2CHOO^* + *$

R224: $CH_2$* + HCOOH* ↔ $CH_2$-CHOOH* + * ↔ $CH_2$CHOOH* + *

R225: $CH_3$* + COOH* ↔ $CH_3$-COOH* + * ↔ $CH_3$COOH* + *

R226: $CH_3$* + HCOO* ↔ $CH_3$-CHOO* + * ↔ $CH_3$CHOO* + *

R227: $CH_3$* + HCOOH* ↔ $CH_3$-CHOOH* + * ↔ $CH_3$CHOOH* + *

R228: CO* + CHO* ↔ OC-CHO* + * ↔ OCCHO* + *

R229: CO* + COH* ↔ OC-COH* + * ↔ OCCOH* + *

R230: CO* + $CH_2$O* ↔ CO-$CH_2$O* + * ↔ CO$CH_2$O* + *

R231: CO* + $CH_2$OH* ↔ OC-$CH_2$OH* + * ↔ OC$CH_2$OH* + *

R232: CO* + CHOH* ↔ OC-CHOH* + * ↔ OCCHOH* + *

R233: CHO* + COH* ↔ OCH-COH* + * ↔ HOCCHO* + *

R234: CHO* + $CH_2$OH* ↔ OCH-$CH_2$OH* + * ↔ OCH$CH_2$OH* + *

R235: CHO* + $CH_2$O* ↔ OC$H_2$-CHO* + * ↔ OC$H_2$CHO* + *

R236: CHO* + CHOH* ↔ OCH-CHOH* + * ↔ OCHCHOH* + *

R237: COH* + CHOH* ↔ HOC-CHOH* + * ↔ HOCCHOH* + *

R238: COH* + $CH_2$O* ↔ HOC-$CH_2$O* + * ↔ HOC$CH_2$O* + *

R239: COH* + $CH_2$OH* ↔ HOC-$CH_2$OH* + * ↔ HOC$CH_2$OH* + *

R240: $CH_2$O* + CHOH* ↔ OC$H_2$-CHOH* + * ↔ OC$H_2$CHOH* + *

R241: $CH_2$O* + $CH_2$OH* ↔ OC$H_2$-$CH_2$OH* + * ↔ OC$H_2$$CH_2$OH* + *

R242: CHOH* + $CH_2$OH* ↔ HOC$H_2$-CHOH* + * ↔ HOC$H_2$CHOH* + *

## 3. Energetics calculated with BEEF-vdW

**Table S1.** BEEF-vdW calculated activation barrier ($E_a$) and reaction energy ($\Delta E$) of elementary steps on Rh(111). The adsorption/desorption processes were considered equilibrated.

| | $E_a$ (eV) | $\Delta E$ (eV) | Prefactor (523K) | | $E_a$ (eV) | $\Delta E$ (eV) | Prefactor (523K) |
|---|---|---|---|---|---|---|---|
| R1 | | -0.54 | | R122 | 0.72 | 0.05 | $6.63\times10^{12}$ |
| R2 | | -1.44 | | R123 | 0.49 | 0.04 | $1.36\times10^{13}$ |
| R3 | 1.24 | -0.01 | $3.70\times10^{13}$ | R124 | 1.05 | -0.80 | $9.97\times10^{13}$ |
| R4 | 1.00 | 0.07 | $4.32\times10^{13}$ | R125 | 0.84 | -0.13 | $1.83\times10^{13}$ |
| R5 | 0.67 | -0.44 | $3.87\times10^{13}$ | R126 | 1.12 | 0.35 | $2.39\times10^{13}$ |
| R6 | 0.58 | 0.41 | $1.32\times10^{13}$ | R127 | 0.70 | -0.27 | $9.51\times10^{12}$ |
| R7 | 0.40 | -0.21 | $4.77\times10^{12}$ | R128 | 1.08 | 0.20 | $3.79\times10^{13}$ |
| R8 | 1.23 | 0.89 | $3.56\times10^{12}$ | R129 | 0.50 | 0.17 | $5.64\times10^{12}$ |
| R9 | 1.79 | 0.69 | $1.23\times10^{13}$ | R130 | 0.99 | 0.46 | $5.49\times10^{12}$ |
| R10 | 0.69 | 0.34 | $1.25\times10^{13}$ | R131 | 0.65 | -0.61 | $1.11\times10^{13}$ |
| R11 | 0.99 | 0.40 | $6.53\times10^{13}$ | R132 | 0.71 | -0.30 | $2.15\times10^{13}$ |
| R12 | 0.67 | -0.13 | $1.85\times10^{13}$ | R133 | 0.79 | 0.32 | $1.46\times10^{13}$ |
| R13 | 0.89 | 0.01 | $2.50\times10^{13}$ | R134 | 0.61 | -0.17 | $1.24\times10^{13}$ |
| R14 | 0.81 | 0.00 | $2.24\times10^{13}$ | R135 | 0.62 | 0.05 | $6.48\times10^{12}$ |
| R15 | 0.90 | 0.25 | $8.57\times10^{12}$ | R136 | 0.76 | 0.25 | $2.66\times10^{12}$ |
| R16 | 1.66 | 0.68 | $1.23\times10^{13}$ | R137 | 0.62 | -0.07 | $1.2\times10^{13}$ |
| R17 | 0.59 | -0.22 | $4.49\times10^{12}$ | R138 | 0.81 | -0.07 | $1.36\times10^{13}$ |
| R18 | 0.87 | 0.51 | $8.80\times10^{11}$ | R139 | 0.69 | -0.55 | $3.3\times10^{11}$ |
| R19 | 0.55 | -0.04 | $2.49\times10^{12}$ | R140 | 0.86 | -0.11 | $1.02\times10^{13}$ |
| R20 | 0.61 | -0.65 | $8.56\times10^{12}$ | R141 | 1.01 | -0.17 | $2.38\times10^{13}$ |
| R21 | 0.63 | -0.04 | $3.63\times10^{12}$ | R142 | 0.86 | -0.06 | $1.67\times10^{13}$ |
| R22 | 0.53 | -0.09 | $1.09\times10^{13}$ | R143 | 0.59 | -0.03 | $6.9\times10^{12}$ |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| R23 | 0.63 | -0.72 | $4.09\times10^{13}$ | R144 | 1.63 | 1.14 | $4.69\times10^{12}$ |
| R24 | 0.53 | 0.27 | $8.60\times10^{12}$ | R145 | 0.81 | 0.41 | $1.86\times10^{13}$ |
| R25 | 0.56 | -0.48 | $8.82\times10^{12}$ | R146 | 0.71 | 0.32 | $8.48\times10^{12}$ |
| R26 | 0.41 | 0.00 | $6.91\times10^{12}$ | R147 | 0.70 | -0.27 | $1.01\times10^{13}$ |
| R27 | 1.21 | 0.25 | $1.35\times10^{13}$ | R148 | 1.00 | 0.33 | $3.1\times10^{13}$ |
| R28 | 0.67 | 0.54 | $1.26\times10^{13}$ | R149 | 0.65 | -0.09 | $7.18\times10^{12}$ |
| R29 | 0.65 | 0.06 | $8.12\times10^{12}$ | R150 | 0.84 | 0.17 | $1.33\times10^{13}$ |
| R30 | 0.82 | 0.47 | $3.53\times10^{12}$ | R151 | 0.67 | 0.04 | $1.22\times10^{13}$ |
| R31 | 0.86 | 0.19 | $9.14\times10^{12}$ | R152 | 1.06 | 0.89 | $2.95\times10^{12}$ |
| R32 | 0.58 | -0.07 | $8.86\times10^{12}$ | R153 | 1.45 | 1.26 | $1.26\times10^{12}$ |
| R33 | 0.57 | -0.37 | $1.13\times10^{13}$ | R154 | 1.05 | 0.99 | $6.97\times10^{12}$ |
| R34 | 0.79 | -0.24 | $3.05\times10^{13}$ | R155 | 0.43 | -0.27 | $1.23\times10^{13}$ |
| R35 | 0.75 | -0.07 | $1.50\times10^{14}$ | R156 | 0.64 | 0.04 | $7.84\times10^{12}$ |
| R36 | 0.59 | 0.18 | $8.65\times10^{12}$ | R157 | 0.93 | -0.13 | $5.11\times10^{13}$ |
| R37 | 0.77 | 0.45 | $1.20\times10^{13}$ | R158 | 0.92 | 0.20 | $2.44\times10^{13}$ |
| R38 | 0.95 | -0.10 | $1.58\times10^{14}$ | R159 | 1.04 | 0.21 | $4.17\times10^{12}$ |
| R39 | 0.73 | 0.03 | $3.89\times10^{12}$ | R160 | 0.80 | -0.01 | $2.38\times10^{13}$ |
| R40 | 1.07 | 0.04 | $7.07\times10^{12}$ | R161 | 0.59 | -0.25 | $8.25\times10^{12}$ |
| R41 | 0.79 | 0.59 | $2.84\times10^{12}$ | R162 | 0.47 | 0.02 | $1.28\times10^{13}$ |
| R42 | 0.60 | -0.06 | $4.71\times10^{12}$ | R163 | 0.93 | -0.13 | $5.11\times10^{13}$ |
| R43 | 0.80 | 0.54 | $5.99\times10^{12}$ | R164 | 0.84 | -0.18 | $1.71\times10^{13}$ |
| R44 | 1.41 | 0.66 | $5.01\times10^{13}$ | R165 | 0.78 | 0.04 | $1.65\times10^{13}$ |
| R45 | 0.44 | -0.24 | $5.50\times10^{12}$ | R166 | 0.93 | -0.01 | $2.94\times10^{13}$ |
| R46 | 1.13 | -0.09 | $1.88\times10^{13}$ | R167 | 1.25 | -0.53 | $1.27\times10^{13}$ |
| R47 | 0.45 | -0.33 | $7.90\times10^{12}$ | R168 | 0.97 | 0.31 | $4.61\times10^{12}$ |
| R48 | 0.55 | 0.10 | $4.98\times10^{12}$ | R169 | 1.85 | -0.61 | $4.5\times10^{13}$ |
| R49 | 0.51 | -0.05 | $5.41\times10^{12}$ | R170 | 1.11 | 0.14 | $7.55\times10^{12}$ |
| R50 | 0.73 | -0.17 | $6.75\times10^{12}$ | R171 | 1.54 | 0.02 | $6.02\times10^{12}$ |
| R51 | 0.88 | 0.04 | $6.17\times10^{12}$ | R172 | 1.73 | -0.23 | $1.95\times10^{13}$ |

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|---|---|---|---|---|---|---|---|
| R52 | 0.67 | 0.04 | $1.39\times10^{13}$ | R173 | 1.22 | -0.45 | $2.02\times10^{13}$ |
| R53 | 0.91 | 0.06 | $2.94\times10^{13}$ | R174 | 1.72 | -0.09 | $2.26\times10^{13}$ |
| R54 | 0.56 | -0.06 | $6.39\times10^{12}$ | R175 | 0.81 | -0.26 | $4.75\times10^{13}$ |
| R55 | 0.43 | -0.39 | $3.08\times10^{12}$ | R176 | 1.35 | 0.34 | $1.08\times10^{13}$ |
| R56 | 0.68 | -0.80 | $1.22\times10^{13}$ | R177 | 1.35 | 0.09 | $1.24\times10^{13}$ |
| R57 | 0.86 | -0.66 | $1.28\times10^{13}$ | R178 | 1.54 | 0.22 | $1.93\times10^{13}$ |
| R58 | 0.85 | -0.69 | $1.72\times10^{13}$ | R179 | 1.56 | -0.01 | $1.44\times10^{13}$ |
| R59 | 0.76 | -0.25 | $1.18\times10^{13}$ | R180 | 1.47 | 0.61 | $5.4\times10^{12}$ |
| R60 | 0.82 | -0.47 | $1.12\times10^{13}$ | R181 | 1.19 | 0.81 | $2.19\times10^{12}$ |
| R61 | 0.82 | -0.99 | $1.12\times10^{13}$ | R182 | 1.64 | 0.44 | $1.2\times10^{13}$ |
| R62 | 1.07 | 0.65 | $3.42\times10^{12}$ | R183 | 0.82 | -0.58 | $3.45\times10^{12}$ |
| R63 | 1.05 | 0.46 | $7.31\times10^{13}$ | R184 | 0.97 | -0.09 | $3.46\times10^{12}$ |
| R64 | 1.62 | -1.31 | $1.70\times10^{13}$ | R185 | 1.51 | -0.19 | $9\times10^{12}$ |
| R65 | 1.59 | 0.02 | $1.90\times10^{13}$ | R186 | 1.73 | 0.07 | $1.53\times10^{13}$ |
| R66 | 1.14 | -0.05 | $4.17\times10^{12}$ | R187 | 1.25 | 0.35 | $1.9\times10^{13}$ |
| R67 | 1.53 | 0.02 | $4.27\times10^{12}$ | R188 | 0.55 | 0.14 | $1.44\times10^{13}$ |
| R68 | 1.00 | -0.61 | $8.66\times10^{12}$ | R189 | 0.85 | -0.30 | $3.7\times10^{12}$ |
| R69 | 1.05 | 0.42 | $8.38\times10^{12}$ | R190 | 1.80 | 0.13 | $1.95\times10^{13}$ |
| R70 | 1.03 | -0.03 | $3.39\times10^{12}$ | R191 | 0.52 | -0.28 | $2.56\times10^{12}$ |
| R71 | 1.48 | 0.36 | $2.93\times10^{12}$ | R192 | 1.06 | 0.08 | $3.71\times10^{12}$ |
| R72 | 1.17 | 0.52 | $7.51\times10^{12}$ | R193 | 0.84 | 0.01 | $3.51\times10^{12}$ |
| R73 | 0.79 | -0.12 | $1.50\times10^{13}$ | R194 | 0.82 | 0.45 | $6.57\times10^{11}$ |
| R74 | 1.20 | 0.51 | $9.15\times10^{12}$ | R195 | 0.84 | 0.01 | $3.4\times10^{12}$ |
| R75 | 0.97 | 0.05 | $7.88\times10^{13}$ | R196 | 0.81 | -0.55 | $1\times10^{13}$ |
| R76 | 0.92 | -0.56 | $8.59\times10^{12}$ | R197 | 0.89 | -0.39 | $5.72\times10^{12}$ |
| R77 | 1.03 | -0.68 | $9.24\times10^{12}$ | R198 | 1.19 | 0.13 | $6.21\times10^{12}$ |
| R78 | 1.40 | 0.96 | $8.27\times10^{12}$ | R199 | 0.63 | -0.09 | $1.82\times10^{13}$ |
| R79 | 0.86 | 0.09 | $5.38\times10^{12}$ | R200 | 0.96 | 0.24 | $6.96\times10^{12}$ |
| R80 | 1.04 | 0.30 | $5.36\times10^{12}$ | R201 | 0.74 | -0.38 | $4.68\times10^{12}$ |

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|---|---|---|---|---|---|---|---|
| R81 | 1.14 | 0.40 | $4.45\times10^{13}$ | R202 | 1.34 | 0.08 | $7.98\times10^{12}$ |
| R82 | 1.09 | 0.15 | $1.12\times10^{13}$ | R203 | 0.90 | 0.72 | $3.83\times10^{12}$ |
| R83 | 1.14 | 0.30 | $1.95\times10^{13}$ | R204 | 1.05 | 0.27 | $7.93\times10^{12}$ |
| R84 | 1.10 | 0.51 | $3.84\times10^{12}$ | R205 | 0.90 | 0.42 | $5.15\times10^{12}$ |
| R85 | 0.63 | -0.38 | $2.89\times10^{12}$ | R206 | 0.96 | 0.45 | $6.42\times10^{12}$ |
| R86 | 1.21 | 0.07 | $2.56\times10^{12}$ | R207 | 0.43 | 0.26 | $1.55\times10^{12}$ |
| R87 | 0.94 | -0.25 | $4.98\times10^{12}$ | R208 | 1.31 | 0.33 | $6.47\times10^{12}$ |
| R88 | 0.72 | -0.58 | $1.80\times10^{12}$ | R209 | 1.48 | 0.28 | $7.57\times10^{12}$ |
| R89 | 1.06 | -0.50 | $1.66\times10^{12}$ | R210 | 0.55 | 0.41 | $2.31\times10^{12}$ |
| R90 | 1.58 | 0.24 | $4.07\times10^{12}$ | R211 | 0.47 | 0.19 | $2.27\times10^{12}$ |
| R91 | 1.05 | -0.11 | $2.28\times10^{12}$ | R212 | 1.22 | 0.01 | $8.48\times10^{12}$ |
| R92 | 1.30 | 0.20 | $6.67\times10^{11}$ | R213 | 1.56 | -0.10 | $2.71\times10^{13}$ |
| R93 | 1.69 | -0.41 | $5.27\times10^{12}$ | R214 | 1.22 | 0.23 | $1.08\times10^{13}$ |
| R94 | 1.09 | -0.45 | $4.88\times10^{12}$ | R215 | 0.23 | -0.10 | $2.08\times10^{13}$ |
| R95 | 1.92 | -1.09 | $1.90\times10^{13}$ | R216 | 0.54 | -0.20 | $2.48\times10^{12}$ |
| R96 | 0.87 | 0.76 | $1.09\times10^{13}$ | R217 | 1.87 | 0.12 | $7.^{13}\times10^{13}$ |
| R97 | 1.43 | 1.22 | $8.73\times10^{11}$ | R218 | 0.85 | -0.14 | $1.08\times10^{13}$ |
| R98 | 0.62 | -0.32 | $1.52\times10^{13}$ | R219 | 0.52 | 0.08 | $1.18\times10^{13}$ |
| R99 | 0.99 | 0.94 | $1.52\times10^{14}$ | R220 | 1.10 | 0.19 | $1.07\times10^{13}$ |
| R100 | 0.50 | -0.04 | $1.99\times10^{13}$ | R221 | 0.99 | 0.56 | $1.12\times10^{13}$ |
| R101 | 1.05 | 0.38 | $1.19\times10^{13}$ | R222 | 0.88 | -0.26 | $7\times10^{12}$ |
| R102 | 0.94 | -0.70 | $5.72\times10^{12}$ | R223 | 1.59 | 1.13 | $2.19\times10^{12}$ |
| R103 | 0.53 | 0.18 | $1.25\times10^{13}$ | R224 | 0.95 | -0.12 | $5.93\times10^{12}$ |
| R104 | 0.46 | 0.25 | $4.33\times10^{12}$ | R225 | 1.37 | 0.27 | $3.76\times10^{12}$ |
| R105 | 0.48 | -0.13 | $9.90\times10^{12}$ | R226 | 2.07 | 0.73 | $2.07\times10^{12}$ |
| R106 | 1.58 | -0.31 | $9.62\times10^{12}$ | R227 | 1.47 | -0.47 | $2.65\times10^{12}$ |
| R107 | 0.69 | -0.15 | $3.81\times10^{12}$ | R228 | 1.38 | 0.96 | $6.59\times10^{12}$ |
| R108 | 1.47 | -0.14 | $3.44\times10^{13}$ | R229 | 1.53 | 1.21 | $2.38\times10^{12}$ |
| R109 | 0.96 | 0.28 | $1.17\times10^{14}$ | R230 | 1.41 | 0.91 | $2.57\times10^{13}$ |

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|---|---|---|---|---|---|---|---|
| R110 | 0.98 | -0.04 | $3.26\times10^{12}$ | R231 | 1.76 | 0.62 | $8.63\times10^{12}$ |
| R111 | 0.42 | -0.17 | $1.51\times10^{13}$ | R232 | 1.41 | 0.66 | $9.47\times10^{12}$ |
| R112 | 0.89 | -0.59 | $6.02\times10^{13}$ | R233 | 1.29 | 0.49 | $2.51\times10^{12}$ |
| R113 | 0.68 | -0.12 | $3.40\times10^{12}$ | R234 | 1.28 | -0.02 | $5.69\times10^{12}$ |
| R114 | 1.53 | 0.98 | $6.54\times10^{11}$ | R235 | 1.09 | 0.29 | $1.35\times10^{13}$ |
| R115 | 0.48 | -0.43 | $7.56\times10^{12}$ | R236 | 0.92 | -0.06 | $5\times10^{12}$ |
| R116 | 1.05 | 0.23 | $3.10\times10^{13}$ | R237 | 1.40 | 0.29 | $1.08\times10^{13}$ |
| R117 | 0.47 | 0.10 | $8.35\times10^{12}$ | R238 | 1.51 | 0.56 | $1.47\times10^{13}$ |
| R118 | 0.64 | 0.28 | $7.29\times10^{12}$ | R239 | 1.50 | 0.38 | $3.64\times10^{12}$ |
| R119 | 0.95 | 0.10 | $1.50\times10^{13}$ | R240 | 1.21 | -0.19 | $9.3\times10^{12}$ |
| R120 | 1.03 | 0.05 | $1.62\times10^{13}$ | R241 | 1.80 | -0.32 | $1.31\times10^{14}$ |
| R121 | 0.70 | 0.18 | $6.83\times10^{12}$ | R242 | 1.22 | -0.33 | $2.72\times10^{12}$ |

## 4. The definition of $F_{DRC}$ and $F_c$

The frequency of the transition state *s* of with maximum DRC, denoted as $F_{DRC}$, can be calculated with the following equation:

$$F_{DRC} = \frac{1}{N_f} \sum_{n=1}^{N_f} \delta\left( s - \arg\max_{s' \in S_a} DRC(n, s') \right) \tag{S1}$$

where $N_f$ is the total number of exchange-correlation functionals generated around BEEF-vdW, $\delta$ denotes the Kronecker delta function. $S_a$ can be regarded as the indexes of all transition states, $DRC(n,s')$ denotes the DRC of the transition state $s'$, calculated using the exchange-correlation functional *n* generated around BEEF-vdW. Arguments of the maxima DRC(*argmaxDRC*) denotes the transition state when its DRC is maximum. Meanwhile, the frequency of intermediates *c* with the maximum coverage, denoted as $F_c$, can be written as:

$$F_c = \frac{1}{N_f} \sum_{n=1}^{N_f} \delta\left( c - \arg\max_{c' \in C_a} Coverage(n, c') \right) \tag{S2}$$

where $C_a$ is the indexes of all intermediates, *Coverage(n,c')* denotes the coverage of the intermediate with index *c',* calculated using the exchange-correlation functional *n* generated around BEEF-vdW. Arguments of the maxima coverage (*argmaxCoverage*) is the intermediate when its coverage is maximum.

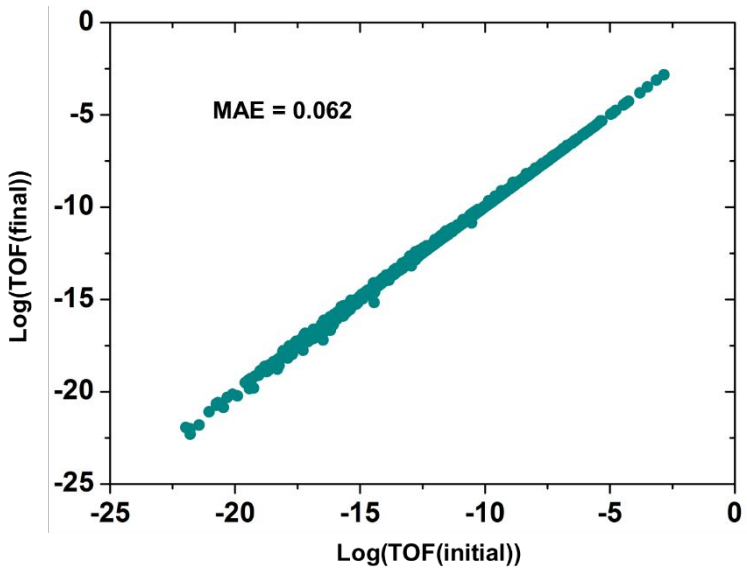


**Figure S1.** Parity plot between the logarithm of TOF after network pruning (TOF(final)) and that before network pruning (TOF(initial)), calculated with BEEF-vdW energies at 523 K and log(pressure/bar) = 1.5.

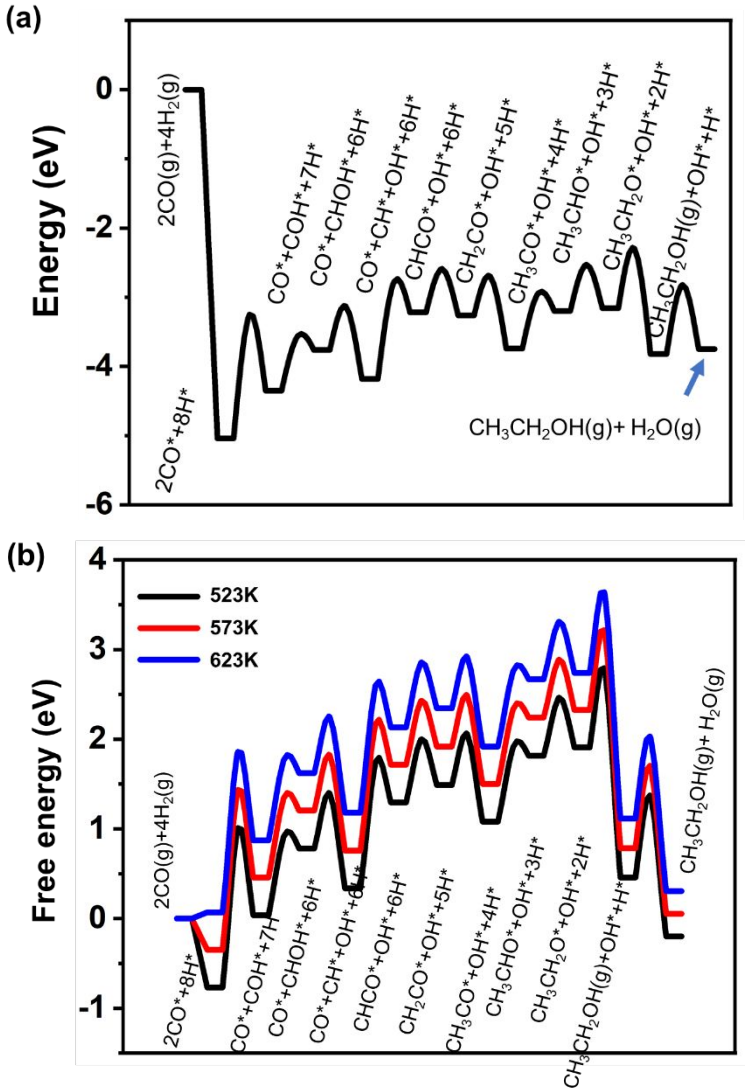


**Figure S2.** Total energy and free energy profiles of CO hydrogenation to $CH_3CH_2OH$ and $H_2O$ over Rh(111). The temperatures considered in the plot of free energy profile are 523, 573 and 623 K.