Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


**Electronic Supplementary Information**

# Theoretical Understandings on the Selectivity of Acrolein Hydrogenation over Silver Surfaces: Non-Horiuti-Polanyi Mechanism is the Key

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**Table S1.** Activation energies (in eV) of hydrogen atoms recombination to hydrogen molecule and hydrogenation of MS4 to enol with atomic and molecular hydrogen obtained with PBE and PBE-TS calculations. All the energies are ZPE corrected. The free energy barriers including entropic effects are presented in bracket.

| | | Ag111 | Ag100 | Ag211 | Ag111-mono |
|---|---|---|---|---|---|
| $2H^* \rightarrow H_2$ | PBE | 1.05 | 0.79 | 0.8 | 0.88 |
| | PBE-TS | 1.03 | 0.80 | 0.79 | 0.82 |
| $CH_3CHCHO^* + H^*$ | PBE | 0.7 | 0.76 | 0.95 | 1.14 |
| $\rightarrow CH_3CHCHOH^*$ | PBE-TS | 0.56 | 0.74 | 0.99 | 1.09 |
| $CH_3CHCHO^* + H_2$ | PBE | / | / | 0.60 (1.36) | 0.47 (1.23) |
| $\rightarrow CH_3CHCHOH^* + H^*$ | PBE-TS | / | / | 0.43 (1.19) | 0.38 (1.14) |

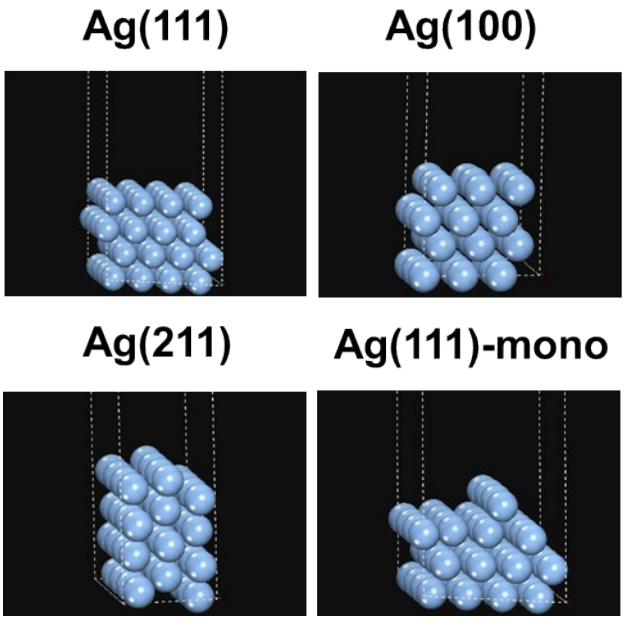


**Figure S1.** Structures of Ag(111), Ag(100), Ag(211) and Ag(111)-mono surfaces.

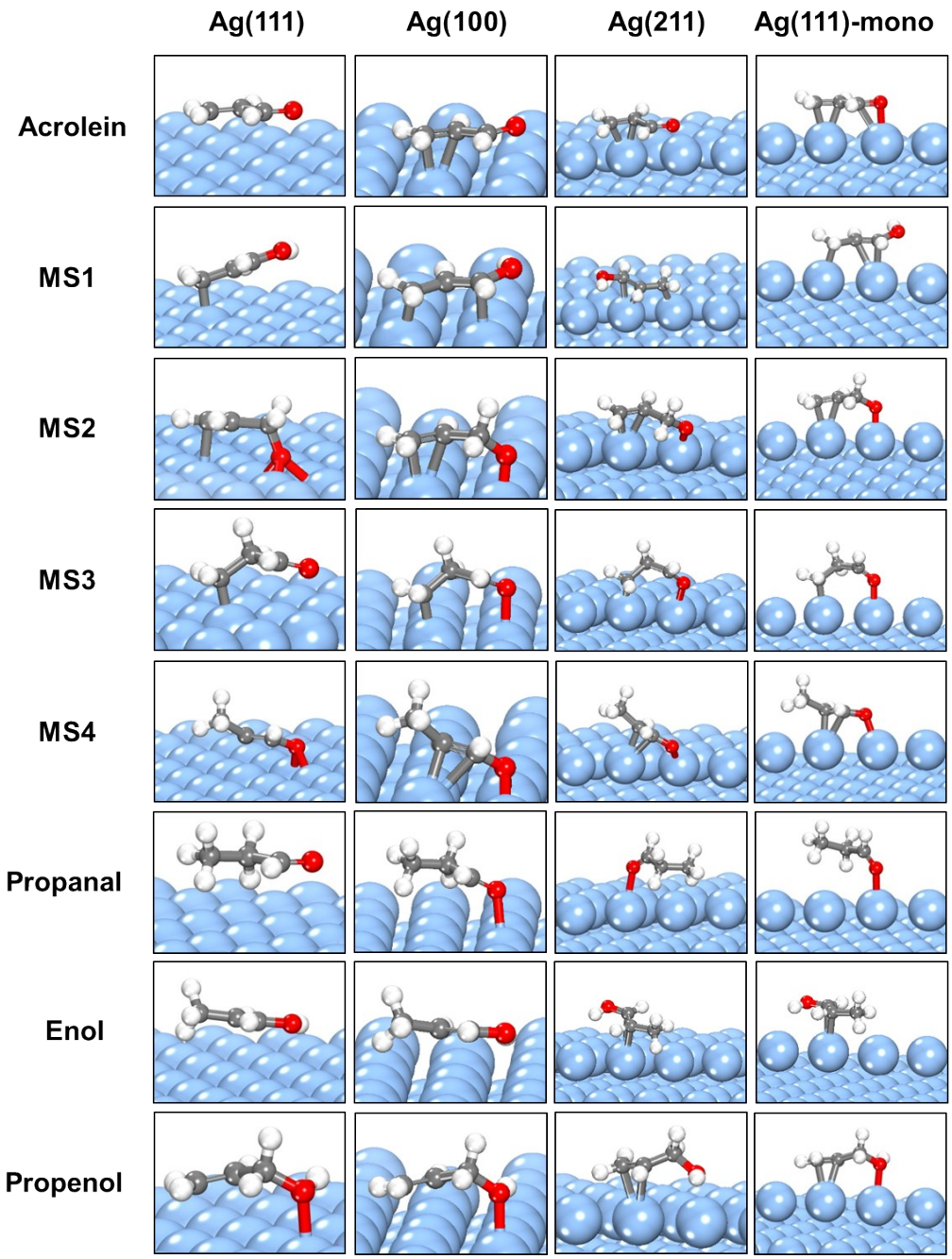


**Figure S2.** Adsorption configurations of acrolein ($C_3H_4O$), MS1 ($CH_2CHCHOH$), MS2 ($CH_2CHCH_2O$), MS3 ($CH_2CH_2CHO$), MS4 ($CH_3CHCHO$), propanal ($CH_3CH_2CHO$), enol ($CH_3CHCHOH$) and propenol ($CH_2CHCH_2OH$) over Ag(111), Ag(100), Ag(211) and Ag(111)-mono surfaces obtained without dispersion corrections. The oxygen, carbon, hydrogen and silver atoms are shown in red, grey, white and light blue, respectively, and this notation is used throughout the paper.

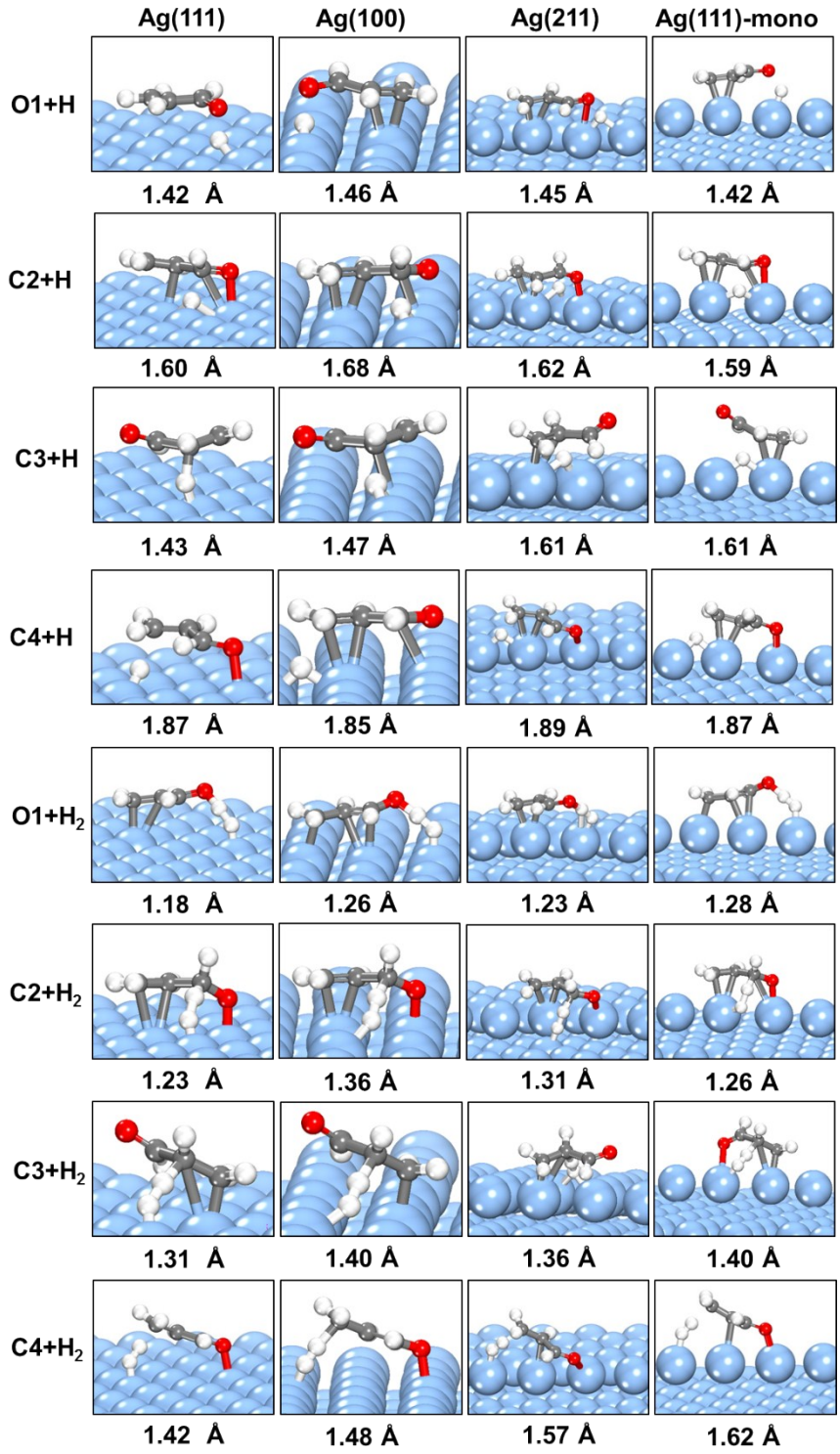


**Figure S3.** Transition state structures of $C_3H_4O$ hydrogenation with atomic and molecular hydrogen obtained without dispersion corrections. O1-H, C2-H, C3-H and C4-H distances at the corresponding transition states are also shown here.

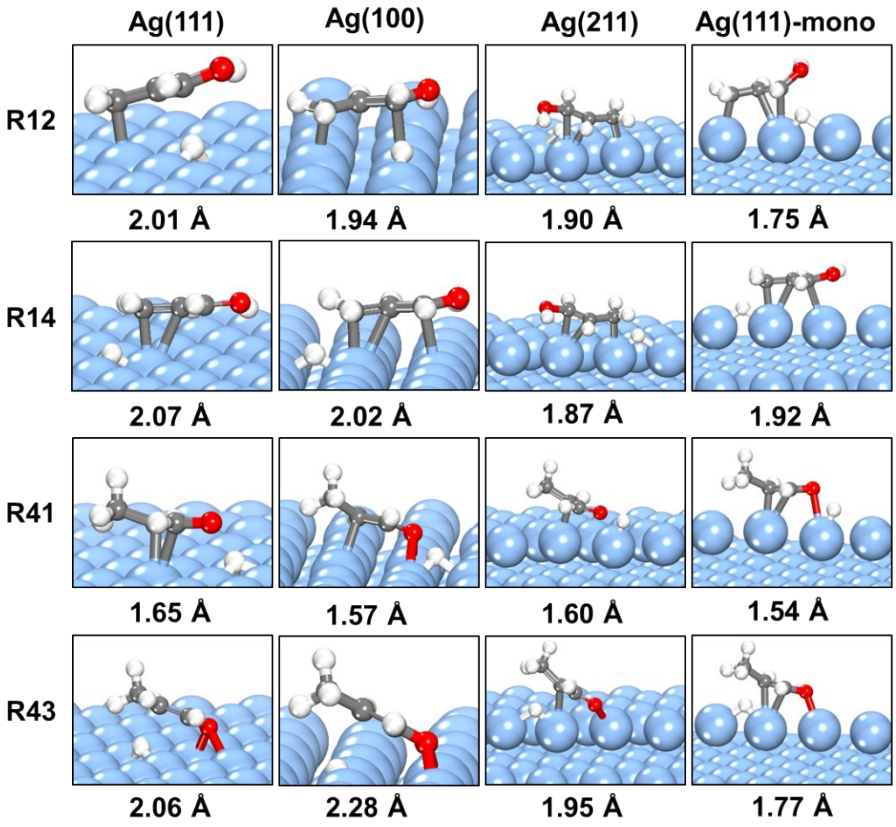


**Figure S4.** Transition state structures of $C_3H_5O$ hydrogenation to propenol (R12), enol (R41 and R14) and propanal (R43) with atomic hydrogen obtained without dispersion corrections. O1-H, C2-H, C3-H and C4-H distances at the corresponding transition states are also shown.

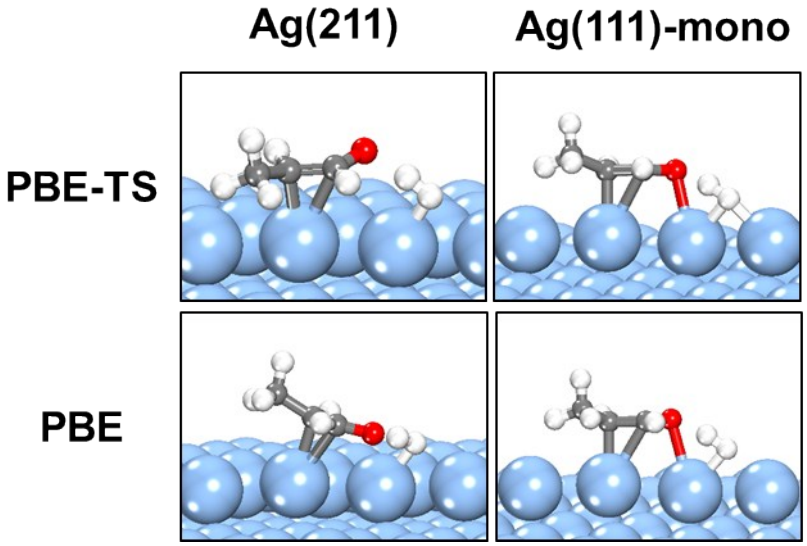


**Figure S5.** Transition state structures of $CH_3CHCHO$ hydrogenation with molecular hydrogen to form enol on Ag(211) and Ag(111)-mono surfaces obtained from PBE and PBE-TS calculations.

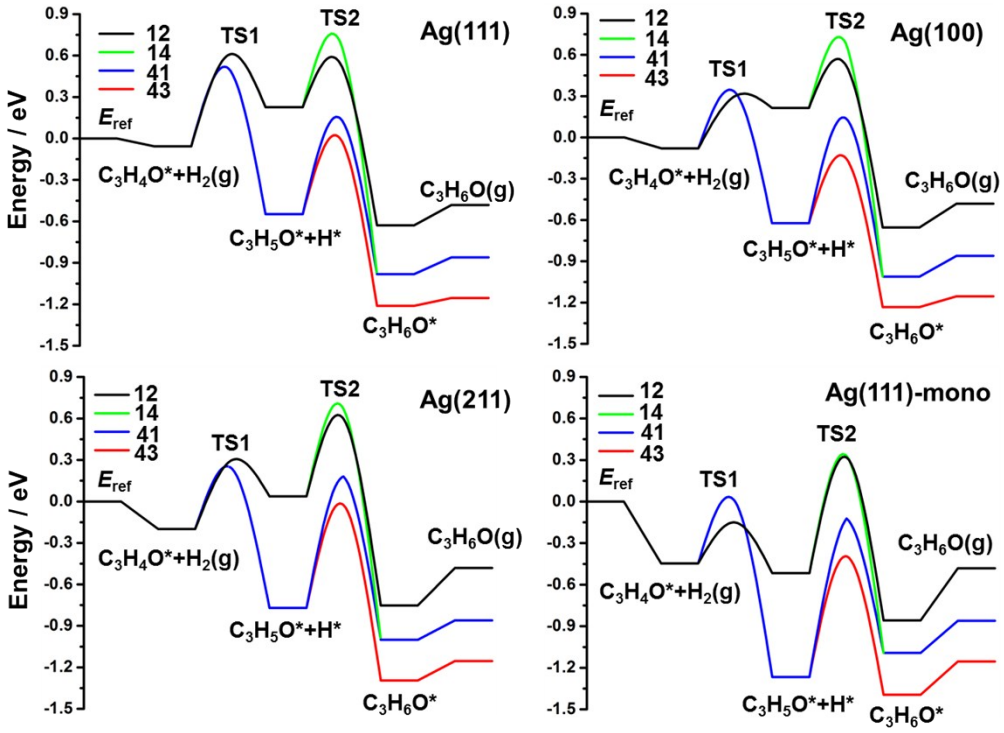


**Figure S6.** Energy profiles of the preferred acrolein hydrogenation pathways to propenol (12), enol (14 and 41) and propanal (43) over Ag(111), Ag(100), Ag(211) and Ag(111)-mono surfaces are obtained from PBE calculations. The gas phase total energy of acrolein + $H_2$ is defined as the reference energy.