Supporting Information

Toward rational catalyst design for Partial Hydrogenation of Dimethyl Oxalate to Methyl Glycolate: A Descriptor-Based Microkinetic Analysis

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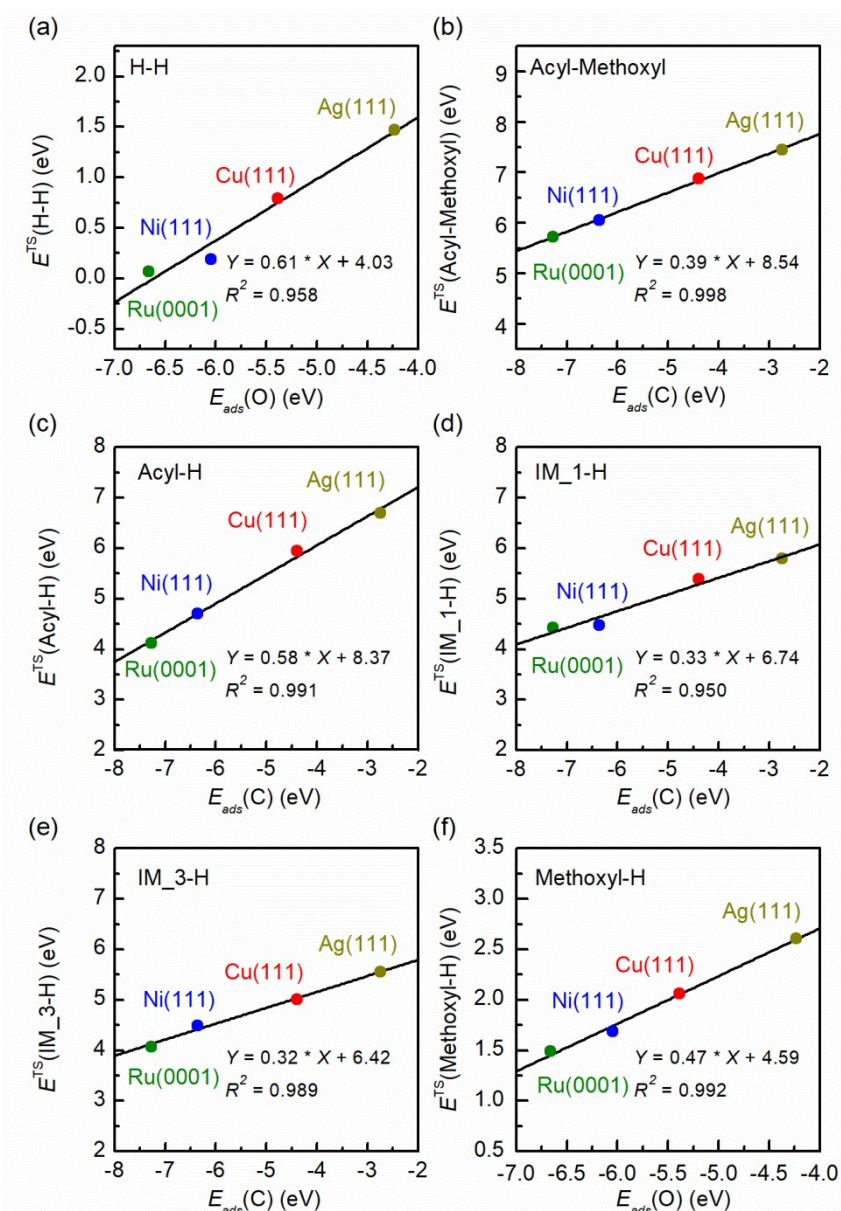## S.1 Linear transition state energy scaling relations

Fig S1. Linear transition state energy scaling relations for the dissociation of (a) H_2 and (b) DMO and the hydrogenation of (c) acyl, (d) IM_1, (e) IM_3, and (f) methoxyl.

S.2 Microkinetic Modelling

The microkinetic model is constructed under the mean-field approximation. Rate expressions have the form:

$$r_i = (k_{f,i} \prod_{j \in P_{IS}} P_j \prod_{\theta \in \theta_{IS}} \theta_j) - (k_{r,i} \prod_{j \in P_{FS}} P_j \prod_{\theta \in \theta_{FS}} \theta_j) \tag{1}$$

where r_i is the rate of elementary step i, $P_{IS/FS}$ are the gas pressures in the initial/final state of step i, and $\theta_{IS/FS}$ are the coverages of intermediates in the initial/final state of step i. The coverages are normalized such that the sum of all coverages for each type of adsorption site is constrained to unity. The reaction rate constants $k_{f/r,i}$ are computed using transition-state theory:

$$k_{f,i} = \frac{k_{BT}}{h} \exp(\frac{-\Delta G_{act,i}}{k_B T}) \tag{2}$$

$$k_{r,i} = \frac{k_B T}{h} \exp(\frac{-(\Delta G_{act,i} - \Delta G_{rxn,i})}{k_B T}) \tag{3}$$

where $\Delta G_{act,i} = G_{TS} - G_{IS}$, $\Delta G_{rxn,i} = G_{FS} - G_{IS}$, k_B and h are Boltzmann's and Planck's constants, respectively, and T is the temperature in Kelvin. G_{IS}, G_{FS} and G_{TS} are the Gibbs free energies of the initial, final, and transition states, respectively. Gibbs free energies are computed as the DFT formation energy plus a thermodynamic correction.

The rate expressions are used to determine the rate of change for all coverages as follows:

$$\frac{d\theta_j}{dt} = \sum_{n \in r_{FS}} s_n r_n - \sum_{n \in r_{IS}} s_n r_n \tag{4}$$

where t is time, $r_{IS/FS}$ is the set of reactions where intermediate j appears in the initial/final state, and s_n is the stoichiometry of intermediate j in reaction n.

The Gibbs free energy of gas-phase species A [DMO(g), MG(g), H$_2$(g), CH$_3$OH(g)] at temperature T and pressure P is given by

$$G_A(T,P) = E_{total,A} + E_{ZPE} + \Delta H°(0 \to T) - TS(T,P)$$

$$= E_{total,A} + E_{ZPE} + \Delta H°(0 \rightarrow T) - TS°(T) + RT \ln\left(\frac{P}{P°}\right) \tag{5}$$

where $E_{total,A}$ is the total energy determined by DFT calculations. E_{ZPE} is the zero-point energy, which is calculated by

$$E_{ZPE} = \sum_{i=1}^{3N-6(5)} \frac{N_A h \nu_i}{2} \tag{6}$$

where N_A is Avogadro's number, h is Plank's constant, ν_i is the frequency of the normal mode, and N is the number of atoms involved in the system. $\Delta H°(0 \rightarrow T)$ is the enthalpy change, which is assumed to be zero. $S°(T)$ is the entropy changer per degree, which is assumed to be 0.00135 eV/K for hydrogen gas and 0.002 eV/K for other gases.

The Gibbs free energy for a species A adsorbed on Ni surface is calculated as

$$G_A(T,P) = E_{total,A} + E_{ZPE} + \Delta U°(0 \rightarrow T) - TS°(T) \tag{7}$$

where the enthalpy change is replaced by the change of internal energy.

The standard internal energy change of adsorption is calculated by

$$\Delta U°(0 \rightarrow T) = \sum_{i=1}^{3N} \frac{N_A h \nu_i e^{-h\nu_i/k_BT}}{1 - e^{-h\nu_i/k_BT}} \tag{8}$$

The standard entropy change ($\Delta S°$) of adsorption is calculated by

$$S°(T) = S°_{vib}(T) = \sum_{i=1}^{3N}\left[-R\ln\left(1 - e^{-h\nu_i/k_BT}\right) + \frac{N_A h \nu_i}{T} \frac{e^{-h\nu_i/k_BT}}{\left(1 - e^{-h\nu_i/k_BT}\right)}\right] \tag{9}$$