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

Supporting Information for

Acetic acid hydrodeoxygenation on molybdenum carbide catalysts

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Supporting Information

S.1 Cyclohexane co-feed for acetic acid HDO on molybdenum carbide catalyst

GC areas of acetic acid HDO products in presence/absence of cyclohexane co-feed is shown in Figure S1 below. The negligible change in GC areas when comparing data recorded with and without cyclohexane in the feed shows that cyclohexane can be used as an internal standard for quantification of reactant and product concentrations during acetic acid HDO.

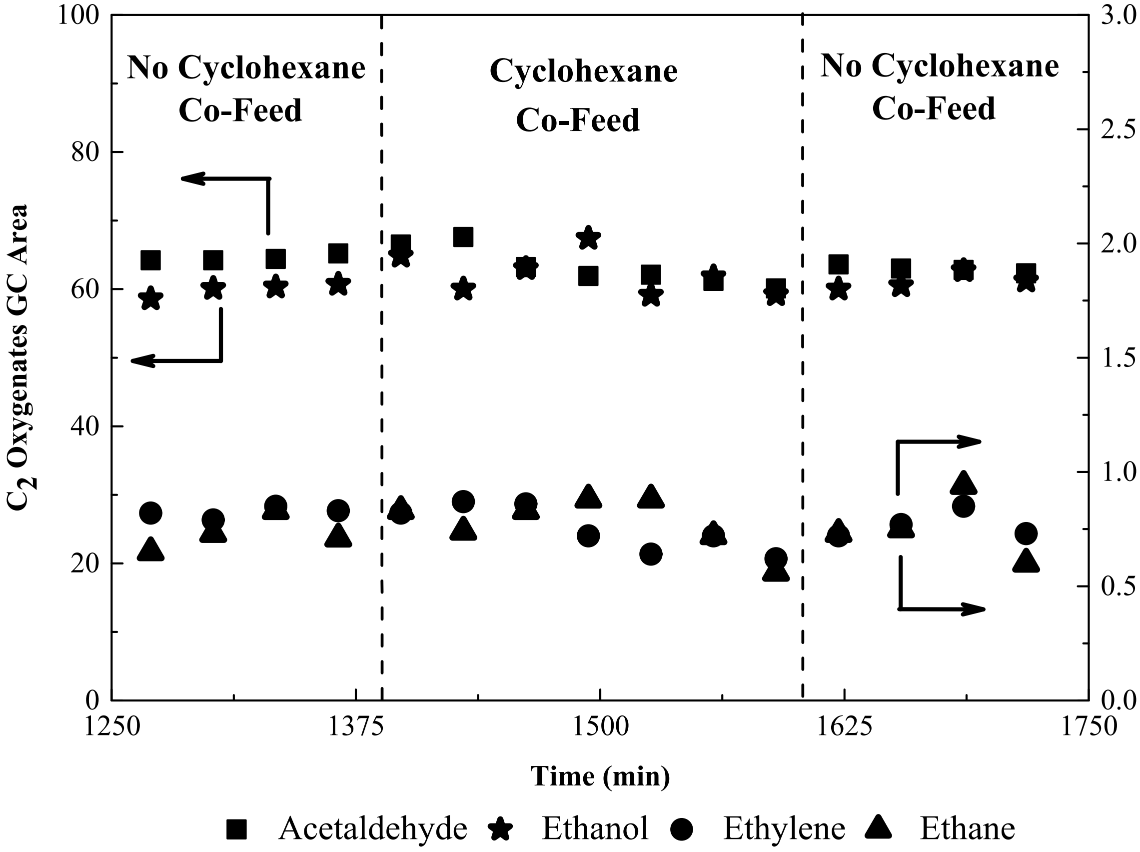


Figure S1. Time on stream evolution of product GC areas of acetic acid HDO in presence/absence of cyclohexane co-feed. Reaction conditions: temperature = 403 K under ambient pressure; feed composition: acetic acid/cyclohexane/H_2 = 0.99 kPa/0.08 kPa/balance; Mo_2C loading ~113 mg.

S.2 Product rank and stability analysis for acetic acid HDO on molybdenum carbide catalyst

Rank and stability of acetic acid HDO products is analyzed using the selectivity vs. conversion plot shown in Figure S2 below. Acetaldehyde is identified as a primary product, while ethanol, ethylene, and ethyl acetate are identified as secondary products. Furthermore, acetaldehyde and ethanol are unstable products while ethylene and ethyl acetate are observed as stable products.

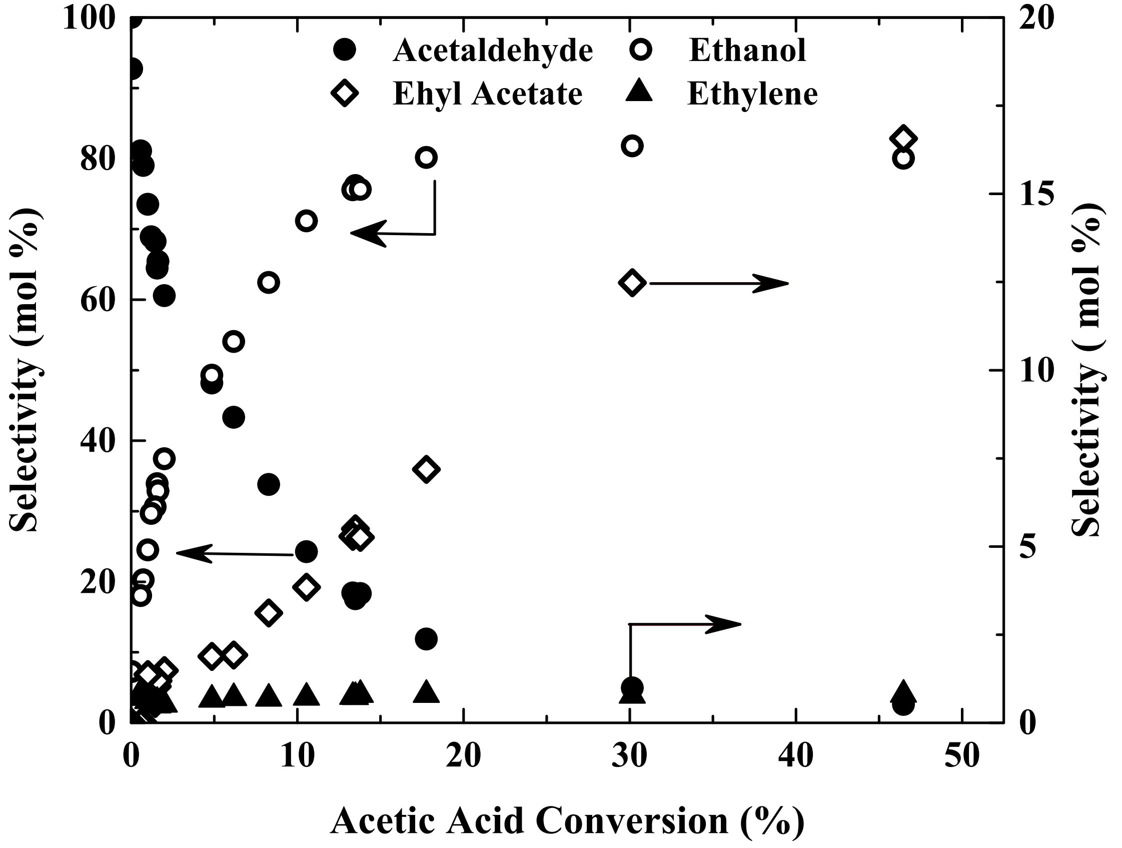
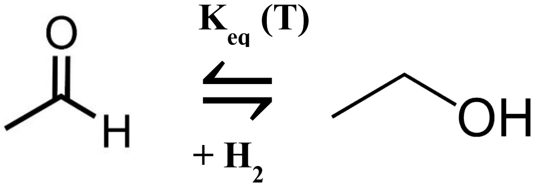


Figure S2. Selectivity (on a molar basis) of acetic acid HDO products on as-synthesized Mo_2C catalyst used in this study with respect to acetic acid conversion. Reaction conditions: temperature = 403 K, pressure = 1 atm, acetic acid/ cyclohexane/ H_2 = 1 kPa/0.07 kPa/balance, total flow rate was varied from 0.33 – 6.17 cm^3 s^{-1} and catalyst loading was 95 mg and 720 mg in two independent experiments where contact time varied from 0.06 – 26 h g_{cat} $g_{acetic\ acid}^{-1}$.

S.3 Acetaldehyde hydrogenation equilibrium calculations

Acetaldehyde hydrogenation to form ethanol is represented below:



The approach to equilibrium can be calculated as follows:

$$\eta = \left(\frac{P_{ethanol}}{P_{acetaldehyde}P_{H_2}}\right)\left(\frac{1}{K_{eq}(T)}\right) \tag{S1}$$

where η is the calculated approach to equilibrium, $P_{ethanol}$, $P_{acetaldehyde}$, and P_{H2} are the reactor effluent partial pressures of ethanol, acetaldehyde, and H_2 in atm, respectively, and K_{eq} is the thermodynamic equilibrium constant of the hydrogenation of acetaldehyde to ethanol.

The thermodynamic equilibrium constant, K_{eq} (T), of hydrogenation of acetaldehyde to ethanol at 403 K is first calculated, in order to determine the approach to equilibrium for acetaldehyde to ethanol, using the following expression:

$$K_{eq}(T) = e^{-\frac{\Delta G_{rxn}}{RT}} \tag{S2}$$

where, ΔG_{rxn} is the free energy change for the acetaldehyde to ethanol reaction at 403 K, calculated as

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} \tag{S3}$$

where, ΔH_{rxn} is the enthalpy change for the acetaldehyde to ethanol reaction at 403 K and ΔS_{rxn} is the entropy change for the acetaldehyde to ethanol reaction. The relevant thermodynamic values calculated at the reaction temperature of 403 K were found to be $\Delta H_{rxn} = -64.09$ kJ mol^{-1}, $\Delta S_{rxn} = -100.27$ J mol^{-1} K^{-1} and $\Delta G_{rxn} = -23.68$ kJ mol^{-1}.[1]

Therefore, using equation S2, K_{eq} (403 K) = 1173.64.

Using equation S1, we calculate the approach to equilibrium for acetaldehyde hydrogenation to ethanol for the space velocity experiments. The approach to equilibrium, η, increased from 1.9 x 10^{-4} to 0.0265 as the contact time increased from 0.2 to 26 h $g_{cat}\ g_{acetic\ acid}{}^{-1}$, indicating that the acetaldehyde to ethanol step is not equilibrated at any condition employed in this study. Similar calculations for acetic acid and H_2 partial pressure variation experiments showed that η varied from 8.7 x 10^{-4} to 1 x 10^{-4} with changes in acetic acid partial pressure (0.14 – 0.97 kPa) and from 2.82 x 10^{-3} to 8 x 10^{-5} with changes in H_2 pressure (11 – 107 kPa). These results show that the second step of acetaldehyde hydrogenation to ethanol is always away from equilibrium under all reactions conditions examined for acetic acid HDO on Mo_2C in this work.

S.4 Heat and mass transfer calculations

The existence of internal mass transfer limitations was estimated by comparing the reaction rate with the diffusion rate following the Weisz-Prater criterion, assuming that the concentration of the reactant on the catalyst pellet surface is close to that in the fluid. The Weisz-Prater criterion is given as:

$$\eta\phi^2 = \frac{r_{obs}\, S\rho_b d_p^{\,2}}{4D_e\, C_s} \tag{S4}$$

where η is the dimensionless effectiveness factor, ϕ is the dimensionless Thiele modulus, r_{obs} is the observed rate of acetic acid HDO in mol s^{-1} g_{cat}^{-1}, S is the surface area of the catalyst in m^2 kg_{cat}^{-1}, ρ_b is the catalyst pellet density in kg_{cat} $(m^3{}_{cat})^{-1}$, d_p is the catalyst crystallite diameter in m, D_e is the effective diffusivity in m^2 s^{-1} ($D_e = D\varepsilon\delta/\tau$, where D is the diffusivity of acetic acid in H_2 at 403 K via Chapman-Enskog Theory[2], ε is the porosity, δ is the constrictivity, and τ is the tortuosity, assumed to be average values of 1.72×10^{-4}, 0.35, 0.8, and 6, respectively), and C_s is the acetic acid concentration on the catalyst pellet surface in mol m^{-3} (assumed to be equal to the acetic acid concentration in the gas fluid). Internal mass transfer limitations are negligible when $\eta\phi^2 \ll 1$, which is confirmed in our reaction system (Table S1).

Table S1. Tabulation of parameters for the calculation of internal mass transfer limitations using the Weisz-Prater criterion for acetic acid HDO on Mo_2C at 403 K.

Parameter	**Value**
r_{obs} (mol $(g_{cat})^{-1}$ s^{-1})	1.50×10^{-7} (highest observed)
S (m^2 kg_{cat}^{-1})	100×10^3
ρ_b (kg_{cat} m^{-3})	759
d_p (m)	2×10^{-6} (based on TEM measurements)[3]
D_e (m^2 s^{-1})[a]	8.03×10^{-6}
C_s (mol m^{-3})	2.86×10^{-3} (9.6 kPa acetic acid at 403 K)
Calculated Weisz-Prater criterion $\eta\phi^2$	**4.96×10^{-6}**

[a] We note that Knudsen diffusivity was not used here because the average diameter of the pores in the catalyst pellet was found to be ~6 x10^{-7} m (from BJH desorption branch), which is much larger than the kinetic diameter of the reactant molecules (kinetic diameter of H_2 and acetic acid is 2.89 x 10^{-12} m and 4.4 x 10^{-10} m respectively).

The existence of internal heat transfer limitations can be estimated by calculating the average temperature within the catalyst pellet following the Anderson criterion[4] which assumes a parabolic temperature profile within the spherical catalyst pellet and a Taylor series expansion of the Arrhenius rate expression around T_s, the temperature of the catalyst pellet surface.

$$\frac{T_{ave}}{T_s} = 1 + \frac{(-\Delta H) r_{obs} S \rho_b d_p^2}{60 \lambda_c T_s} \tag{S5}$$

where T_{ave} is the average temperature within the catalyst pellet in K, T_s is the temperature on the catalyst pellet surface in K (assumed to be equal to the gas phase temperature), ΔH is the reaction enthalpy in J mol^{-1}, and λ_c is the thermal conductivity of the catalyst particle in W m^{-1} K^{-1}. Calculations from Table S2 showed that the average temperature in the catalyst particle was very close (T_{ave}/T_s = 1 – 3.32 x 10^{-15}) to the temperature on the catalyst surface during acetic acid HDO at 403 K.

Table S2. Tabulation of parameters for the calculation of internal heat transfer limitation using Anderson criterion for acetic acid HDO on Mo_2C at 403 K.

Parameter	Value
ΔH (J mol^{-1})	24.7 x 10^3
r_{obs} (mol $(g_{cat})^{-1}$ s^{-1})	1.50 x 10^{-7}
S (m^2 kg_{cat}^{-1})	100 x 10^3
ρ_b (kg_{cat} m^{-3})	759
d_p (m)	2 x 10^{-6} (based on TEM measurements)[3]
λ_c (W m^{-1} K^{-1})	140 (Thermal conductivity of Mo_2C)
T_s (K)	403
Calculated T_{ave}/T_s	**1 – 3.32 x 10^{-15}**

The concentration of acetic acid on the surface of the catalyst particle is approximated via Mears's criteria,[5] which is a mass balance around a spherical catalyst particle.

$$\frac{C_s}{C_b} = 1 - \frac{r_{obs} S \rho_b d_p}{6 k_g C_b} \tag{S6}$$

where C_s is the acetic acid concentration on the catalyst surface in mol m^{-3}, C_b is the acetic acid concentration in the gas fluid in mol m^{-3}, and k_g is the external mass transfer coefficient in m s^{-1}.

In a similar manner, the temperature gradient between the catalyst pellet surface and the gas fluid can be estimated via an energy balance around the spherical catalyst pellet.

$$\frac{T_s}{T_b} = 1 + \frac{(-\Delta H) r_{obs} S \rho_b d_p}{6 h_g T_b} \tag{S7}$$

where T_s is the temperature of the catalyst pellet surface in K, T_b is the temperature of the gas in K, and h_g is the heat transfer coefficient between the gas phase and the catalyst pellet surface in W m^{-2} s^{-1}. Calculations from Table S3 show that the external concentration and temperature gradients were negligible under the reaction conditions used in this work.

Table S3. Tabulation of parameters for the calculation of external heat and mass transfer limitations using Mears's criteria for acetic acid HDO on Mo_2C at 403 K.

Parameter	**Value**
ΔH (J mol^{-1})	24.7 x 10^{3}
r_{obs} (mol (g_{cat})$^{-1}$ s^{-1})	1.50 x 10^{-7}
S (m^{2} kg$_{cat}^{-1}$)	100 x 10^{3}
ρ_b (kg$_{cat}$ m^{-3})	759
d_p (m)	3 x 10^{-4} (based on average pellet mesh size of 180 – 425 μm)
k_g (m s^{-1})[a]	7.51 x 10^{-2}
h_g (W m^{-2} s^{-1})[b]	1592.7
C_b (mol m^{-3})	2.86 x 10^{-3}
T_s (K)	403
Calculated C_s/C_b	**1 – 2.65 x 10^{-2}**
Calculated T_s/T_b	**1 – 2.19 x 10^{-7}**

[a]: Estimated from Sh (Sherwood number) = $k_g d_p/D_e$ = 2.8 from Frossling correlation $Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$ with Re (Reynolds number) = $U_b d_p/\nu_g$ = 0.24 where U_b = superficial gas velocity = 0.134 m s^{-1} (total volumetric flow rate (1.67 cm^{3} s^{-1}) divided by reaction cross sectional area (0.13 cm^{2}) and void fraction (0.4)), ν_g = kinematic viscosity of

gas = 1.68 x 10^{-4} m^2 s^{-1} (estimated as kinematic viscosity of hydrogen at 403 K), and Sc (Schmidt number) = ν_g/D_e = 20.9.

[b]: Estimated from Nu (Nusselt number) = $h_g d_p/\lambda_g$ = 2.03 where λ_g = thermal conductivity of gas = 0.235 W m^{-1} K^{-1} (estimated from value of hydrogen at 403 K) from Ranz-Marshall correlation $Nu = 2 + 0.6 Re^{1/2} Pr^{1/3}$ with Re (Reynolds number) = 0.24 and Pr (Prandtl number) = 1.13 x 10^{-3} (estimated as Prandtl number of hydrogen at 403 K).

The bed-wise heat transfer limitations were checked using the Mears's criterion given as

$$\frac{\Delta H * R''R_0^2}{k_e Tw} < \frac{0.4 * R * Tw}{E\,[1 + \frac{8 * r_p}{R0 * (Biot)w}]} \qquad \text{(S8)}$$

where, T_w is the temperature of the reactor wall in K, R" is reaction rate per unit bed volume in mol sec^{-1} m^{-3}, R_0 is radius of reactor tube in m, R is ideal gas constant in J mol^{-1} K^{-1}, k_e is the thermal conductivity of catalyst particle in W m^{-1} K^{-1}, E is the Activation energy of the acetic acid HDO obtained experimentally, and r_p is the average particle radius in m. Calculations from Table S4 show that the bed-wise heat transfer limitations were negligible under the reaction conditions used in this work.

Table S4. Tabulation of parameters for the calculation of bed-wise heat transfer limitations using Mears's criteria for acetic acid HDO on Mo_2C at 403 K.

Parameter	**Value**
ΔH (J mol^{-1})	24.7 x 10^3
R" (mol sec^{-1} m^{-3})	0.114
R_0 (m)	2 x 10^{-3}
R (J mol^{-1} K^{-1})	8.314
r_p (m)	1.5 x 10^{-4} (based on average pellet mesh size of 180 – 425 μm)
k_e (W m^{-1} K^{-1})	140
E (kJ mol^{-1})	68
$Biot_w$	3.21 x 10^{-4}
T_w (K)	403
Calculated $\frac{\Delta H * R''R_0^2}{k_e Tw}$	**1.99 x 10^{-7}**

Calculated	$\mathbf{\dfrac{0.4 * R * Tw}{E\,[1 + \dfrac{8 * rp}{R0 * (Biot)w}]}}$	**1.06 x 10^{-5}**

S.5 Derivation of rate dependence for acetic acid HDO schemes

The detailed derivations for the two plausible reaction schemes proposed for acetic acid HDO on Mo_2C are discussed below.

S.5.1 Scheme 1

R = CH_3

$$H_2 + 2\,S_1 \xleftrightarrow{K_1} 2\,H\text{-}S_1 \qquad (1)$$

$$RCOOH + S_2 \xleftrightarrow{K_2} RCOOH\text{-}S_2 \qquad (2)$$

$$RCOOH\text{-}S_2 + H\text{-}S_1 \xrightarrow{k_3} RC(OH)OH\text{-}S_2 + S_1 \qquad (3)$$

$$RC(OH)OH\text{-}S_2 + S_2 \xleftrightarrow{K_4} RCO\text{-}S_2 + H_2O\text{-}S_2 \qquad (4)$$

$$RCO\text{-}S_2 + H\text{-}S_1 \xleftrightarrow{K_5} RCHO\text{-}S_2 + S_1 \qquad (5)$$

$$H_2O\text{-}S_2 \xleftrightarrow{K_6} H_2O + S_2 \qquad (6)$$

$$RCHO\text{-}S_2 \xleftrightarrow{K_7} RCHO + S_1 \qquad (7)$$

$$RCOOH + H_2 \longrightarrow RCHO + H_2O$$

Considering step (3) to be the rate limiting step, the rate of acetaldehyde formation can be expressed as

$$r_{RCHO} = k3\ [H - S1][RCOOH - S2] * \frac{Z}{L1} \tag{S9}$$

where k_3 represents the forward rate constant, $z[H–S_1]/L_1$ represents the probability of finding adjacent [R-COOH-S_2] surface species to [H-S_1] species, L_1 represents the total number of active sites S_1, and [R-COOH-S_2] and [H-S_1] denote surface concentrations of dissociated hydrogen on site S_1 and acetic acid adsorbed on S_2, respectively. Since all the other steps are assumed to be in quasi-equilibrium, so

$$[H - S_1] = \sqrt{K_1}\,[S_1][H_2]^{0.5} \tag{S10}$$

$$[RCOOH - S_2] = K_2[RCOOH][S_2] \tag{S11}$$

The site balances for S_1 and S_2 give

$$L_1 = [S_1] + [H - S_1] \tag{S12}$$

$$L_2$$
$$= [S_2] + [RCOOH - S_2] + [RC(OH)(OH) - S_2] + [RCO - S_2] + [H_2O - S_2] + [RC$$
$$] \tag{S13}$$

Assuming that the most abundant reactive intermediate (MARI) for site 1 (S_1) is empty sites and the coverage of the adsorbed acetic acid intermediate, R-COOH-S_2, is much higher than that for other species adsorbed on S_2 sites,

$$L_1 \approx [S_1] \tag{S14}$$

$$L_2 \approx [RCOOH - S_2] \tag{S15}$$

Therefore, from equations S11 and S15,

$$[S_2] = \frac{L_2}{K_2[RCOOH]} \tag{S16}$$

Substituting the expression of [R-COOH-S_2], [H-S_1], [S_1] and [S_2] derived above, the rate dependence for acetaldehyde formation with half order in H_2 and zero order in acetic acid can be obtained by combining equations S9, S10, S14, and S15, to get:

$$\mathrm{rRCHO} = k_3\sqrt{K_1}\,L_1[H_2]^{0.5}\,L_2 * \frac{Z}{L_1} \tag{S17}$$

$$\mathbf{rRCHO = k_3\sqrt{K_1}\,z\,L_2\,[H_2]^{0.5}[RCOOH]^{0}} \tag{S18}$$

S.5.2 Scheme 2

R = CH_3

$$H_2 + 2\,S_1 \xleftrightarrow{\mathbf{K_1}} 2\,H\text{-}S_1 \tag{1}$$

$$RCOOH + S_2 \xleftrightarrow{\mathbf{K_2}} RCOOH\text{-}S_2 \tag{2}$$

$$RCOOH\text{-}S_2 + S_2 \xleftrightarrow{\mathbf{K_3}} RCO\text{-}S_2 + HO\text{-}S_2 \tag{3}$$

$$RCO\text{-}S_2 + H\text{-}S_1 \xrightarrow{\mathbf{k_4}} RCHO\text{-}S_2 + S_1 \tag{4}$$

$$RCHO\text{-}S_2 \xleftrightarrow{\mathbf{K_5}} RCHO + S_2 \tag{5}$$

$$HO\text{-}S_2 + H\text{-}S_1 \xleftrightarrow{\mathbf{K_6}} H_2O\text{-}S_2 + S_1 \tag{6}$$

$$H_2O\text{-}S_2 \xleftrightarrow{\mathbf{K_7}} H_2O + S_2 \tag{7}$$

$$RCOOH + H_2 \longrightarrow RCHO + H_2O$$

Considering step (4) to be the rate limiting step, the rate of acetaldehyde formation can be expressed as

$$\mathrm{rRCHO} = k_4\,[\mathrm{H - S_1}][\mathrm{RCO - S_2}] * \frac{Z}{L_1} \tag{S19}$$

where k_4 represents the forward rate constant, $z[\mathrm{H{-}S_1}]/L_1$ represents the probability of finding adjacent [R-CO-S_2] surface species to [H-S_1] species, L_1 represents the total number of active sites S_1, and [R-CO-S_2] and [H-S_1] denote surface concentrations of dissociated hydrogen on site S_1 and acetic acid adsorbed on S_2, respectively. Since all the other steps are assumed to be in quasi-equilibrium, so

$$[\mathrm{H - S_1}] = \sqrt{K_1}\,[\mathrm{S_1}][\mathrm{H_2}]^{0.5} \tag{S20}$$

Step (3), (6) and (7) give,

$$[\mathrm{RCOOH - S_2}] = K_2\,[\mathrm{RCOOH}][\mathrm{S_2}] \tag{S21}$$

$$[\mathrm{RCO - S_2}] = \frac{K_3K_2\,[\mathrm{RCOOH}][\mathrm{S_2}]^2}{[\mathrm{HO - S_2}]} \tag{S22}$$

$$[\mathrm{HO - S_2}] = \frac{[\mathrm{H_2O - S_2}][\mathrm{S_1}]}{K_6\,[\mathrm{H - S_1}]} \tag{S23}$$

$$[\mathrm{H_2O - S_2}] = \frac{[\mathrm{H_2O}][\mathrm{S_2}]}{K_7} \tag{S24}$$

Combining equations S24, S23, and S20 gives,

$$[\mathrm{HO - S_2}] = \frac{[\mathrm{H_2O}][\mathrm{S_2}][\mathrm{S_1}]}{K_7K_6\sqrt{K_1}\,[\mathrm{S_1}][\mathrm{H_2}]^{0.5}} \tag{S25}$$

Combining equations S25 and S22 gives,

$$[\mathrm{RCO - S_2}] = \frac{K_3K_2[\mathrm{RCOOH}][S_2]^2K_7K_6\sqrt{K_1}\,[S_1][H_2]^{0.5}}{[H_2O][S_2][S_1]} \tag{S26}$$

Combining equations S19, S20 and S26 gives,

$$\mathrm{rRCHO} = \frac{k_4\sqrt{K_1}\,[S_1][H_2]^{0.5}K_3K_2[\mathrm{RCOOH}][S_2]^2K_7K_6\sqrt{K_1}\,[S_1][H_2]^{0.5}}{[H_2O][S_2][S_1]} * \frac{Z}{L_1}$$

or,

$$\mathrm{rRCHO} = \frac{k_4K_1K_3K_2K_7K_6[\mathrm{RCOOH}][K_2][S_1][S_2]}{[H_2O]} * \frac{Z}{L_1} \tag{S27}$$

The site balances for S_1 and S_2 give,

$$L_1 = [S_1] + [\mathrm{H - S_1}] \tag{S28}$$

$$L_2 = [S_2] + [\mathrm{RCOOH - S_2}] + [\mathrm{RCO - S_2}] + [\mathrm{HO - S_2}] + [\mathrm{RCHO - S_2}] + [\mathrm{H_2O - S_2}] \tag{S29}$$

Assuming that the most abundant reactive intermediate (MARI) for site 1 (S_1) is empty sites and the coverage of the adsorbed acetic acid intermediate, R-CO-S_2, is much higher than that for the other species adsorbed on S_2 sites,

$$L_1 \approx [S_1] \tag{S30}$$

$$L_2 \approx [\mathrm{RCO - S_2}] \tag{S31}$$

Therefore, from equation S26 and equation S31,

$$[S_2] = \frac{L_2[H_2O]}{K_3K_2K_7K_6\sqrt{K_1}[\mathrm{RCOOH}][H_2]^{0.5}} \tag{S32}$$

Substituting the expression of [R-CO-S_2], [H-S_1], [S_1] and [S_2] derived above, the rate dependence for acetaldehyde formation with half order in H_2 and zero order in acetic acid can be obtained by combining equations S27, S30, and S32, to get:

$$rRCHO = k_4\sqrt{K_1}\, L_1[H_2]^{0.5}\, L_2 \; * \; \frac{Z}{L_1} \tag{S33}$$

$$\mathbf{rRCHO = k_4\sqrt{K_1}\, z\, L_2[H_2]^{0.5}[RCOOH]^0} \tag{S34}$$

S.6 Site requirements for acetic acid HDO on Mo_2C catalysts

Acetic acid HDO turnover frequency variation with DMPA co-feed partial pressure where the amount of DMPA adsorbed is calculated using the average residence time, t_2, shown in Figure 8(b) in the main text.

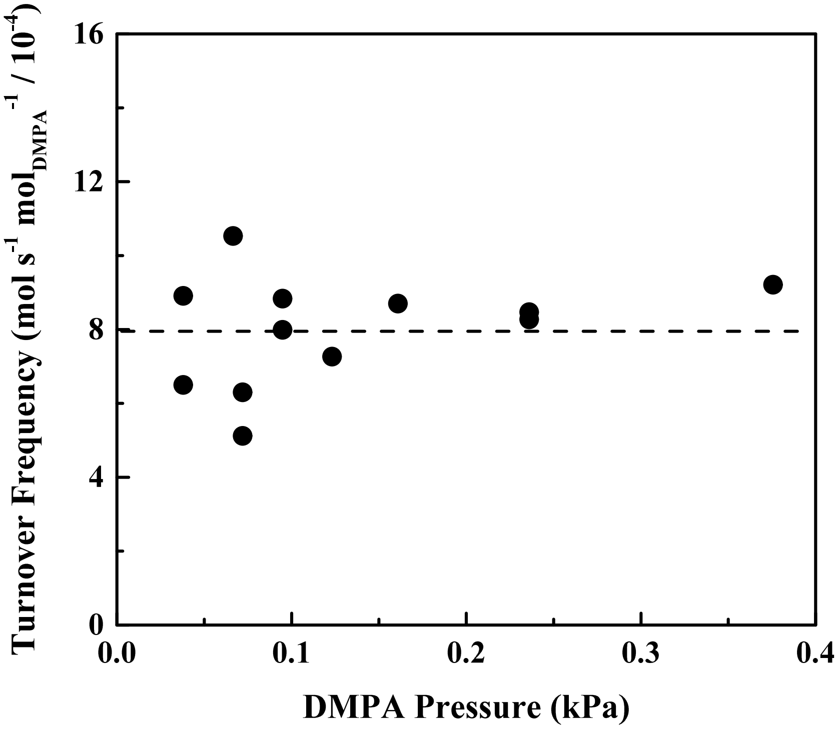


Figure S3. Turnover frequency (TOF) of acetic acid HDO, determined by in-situ DMPA titration, as a function of DMPA pressure (varied 0.04 – 0.38 kPa). Reaction conditions: temperature = 403 K under ambient pressure; feed composition: acetic acid/H_2 = 0.51 kPa/balance; Mo_2C loading ~180 mg. The amount of DMPA adsorbed was calculated using the average residence time, t_2, as shown in Figure 8(b). Acetic acid conversion was always 5.0 – 7.0 % at steady state in absence of DMPA co-feed.

Section S.7: Acetic acid HDO kinetics

Acetic acid HDO rate variation with acetic acid conversion (<10%) as obtained by varying catalyst mass and total flow rate in two independent experiments. Acetic acid HDO rates were found to be invariant with acetic acid conversion demonstrating that HDO products do not have any measurable kinetic effects on acetic acid deoxygenation to acetaldehyde under the reaction conditions reported in this work.

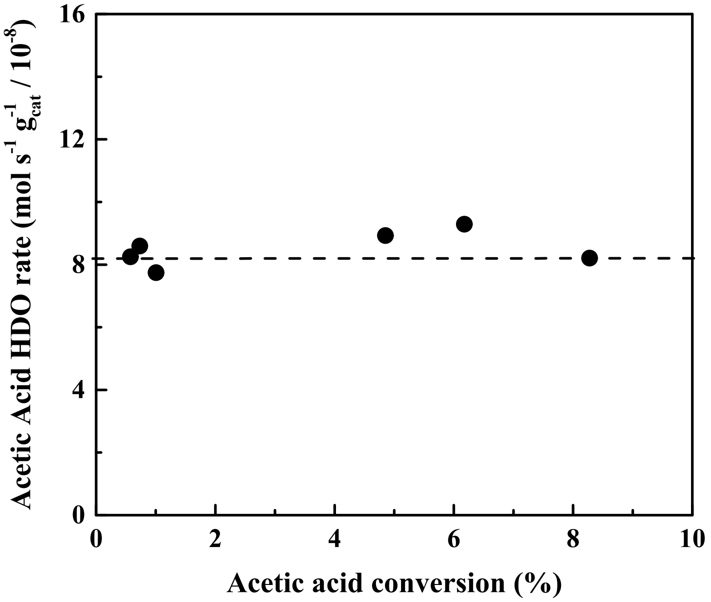


Figure S4. Acetic acid HDO rate as a function of acetic acid conversion. A range of acetic acid conversion was achieved by adjusting the catalyst mass (95 mg and 720 mg in two independent experiments) and total flow rate (3.37 – 6.17 cm^3 s^{-1}) at temperature = 403 K, pressure = 1 atm, acetic acid/ cyclohexane/ H_2 = 1 kPa/0.07 kPa/balance. Dashed line is included as a guide to the eye.

Section S.8: X-ray photoelectron spectroscopy of Mo_2C catalysts

C 1s and O1s of Mo_2C catalysts before and after the acetic acid HDO reaction are shown below.

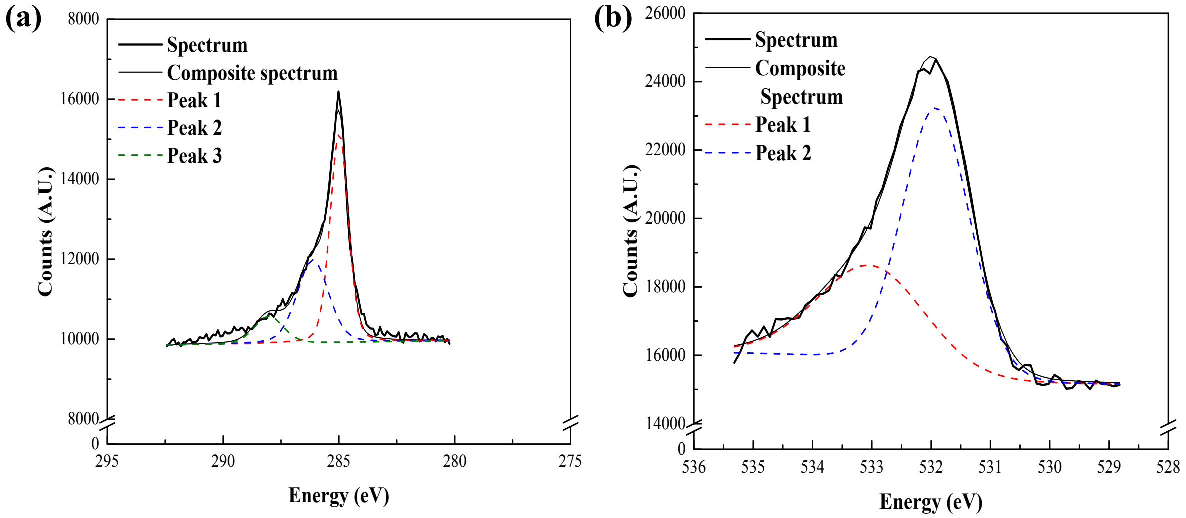
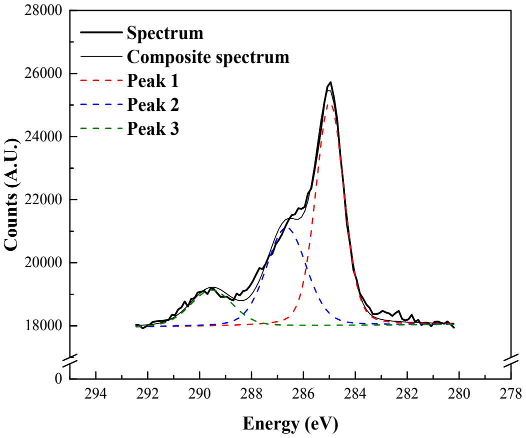


Figure S5. X-ray photoelectron spectrum (XPS) of (a) C 1s and (b) O 1s regions of Mo_2C catalysts before acetic acid HDO reaction.

(a)


Spectrum
Composite spectrum
Peak 1
Peak 2
Peak 3
Counts (A.U.)
28000
26000
24000
22000
20000
18000
0
294
292
290
288
286
284
282
280
278
Energy (eV)

(b)

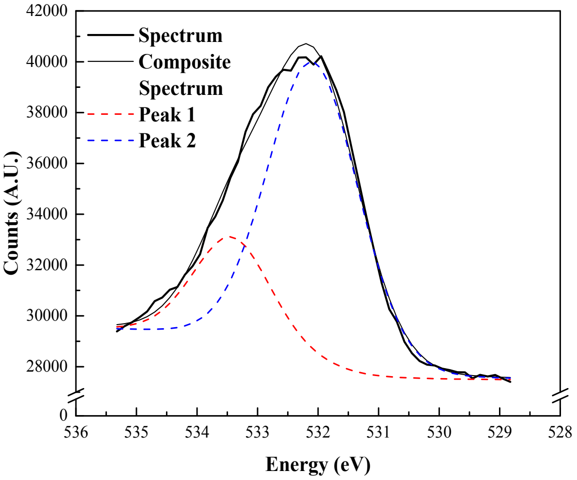

Spectrum
Composite Spectrum
Peak 1
Peak 2
Counts (A.U.)
42000
40000
38000
36000
34000
32000
30000
28000
0
536
535
534
533
532
531
530
529
528
Energy (eV)

Figure S6. X-ray photoelectron spectrum (XPS) of (a) C 1s and (b) O 1s regions of Mo_2C catalysts after acetic acid HDO reaction for 30 h time-on-stream.

References

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