Discovery of a New Solvent Co-Catalyzed Mechanism in Heterogeneous Catalysis: A First Principles Study with Molecular Dynamics on Acetaldehyde Hydrogenation on Birnessite

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Table of Contents

S1 Computational Details ........................................................................................................ 2
  S1.1 Traditional Mechanism Calculations .............................................................................. 2
  S1.2 Solvent Co-catalyzed Mechanism Calculations ........................................................... 3
S2 Optimization of the Birnessite Surface ............................................................................. 4
S3 Initial Structure .................................................................................................................. 5
S4 Investigation of the non-Horiuti-Polanyi Mechanism ..................................................... 8
S4 Investigation of the Horiuti-Polanyi Mechanism ............................................................. 9
S5 Investigation of the Coordination Mechanism ............................................................... 11
S6 Investigation of the Solvent Co-catalyzed Mechanism by AIMD and Umbrella Sampling ................................................................................................................................. 12
Reference ................................................................................................................................ 18
S1 Computational Details

All calculations in this paper were carried out using the Perdew-Burke-Ernzehof (PBE)\(^1\) functional conducted using the Vienna ab initio Simulation Package (VASP). The project-augmented wave (PAW) method was used to represent the core–valence interaction.\(^2,3\) The Brillouin zone was sampled with k-points \(6 \times 6 \times 6\) for lattice parameters optimisation whilst optimisations using the expanded supercell were carried out using a k-point mesh of \(1 \times 1 \times 1\). A cut-off energy of 400 eV was used for total energy calculations for plane wave basis sets to expand the valence electron states.

S1.1 Traditional Mechanism Calculations

For the investigation of traditional mechanism including the Horiuti-Polanyi mechanism, non-Horiuti-Polanyi mechanism, and the coordination mechanism, the upper half of the substrate layers and adsorbates were optimized while the bottom layer was fixed. A 15 Å vacuum layer was built above all the surfaces. The gas-phase molecules, including H\(_2\) and acetaldehyde, were placed in a \((10 \times 10 \times 10)\) Å\(^3\) cubic box to obtain the total energies. To calculate the free chemisorption energy of the species, the total energies were thermodynamically corrected using the standard formulas of statistical thermodynamics.\(^4,5\) Thermodynamic corrections are applied on all adsorption and transition states using DFT-based vibrational frequencies. The zero-point energy (ZPE) correction was calculated as:

\[
ZPE = \sum_i \frac{\hbar v_i}{2}
\]

where \(\hbar\) is Planck’s constant and the standard thermal energy contribution is calculated as

\[
U = RT \sum_i \frac{\hbar v_i / K_B}{e^{\hbar v_i / K_B T} - 1}
\]

where \(K_B\) is the Boltzmann constant and \(R\) is the gas constant. The vibrational entropy is given by

\[
S = R \sum_i \left[ \frac{\hbar v_i / K_B}{e^{\hbar v_i / K_B T} - 1} - \ln \left( 1 - e^{-\hbar v_i / K_B T} \right) \right]
\]

The Gibbs free energy can be achieved by adding the thermodynamic corrections of zero-point-energy (ZPE), thermal energy (U) and entropy (S) derived from vibrational partition function as

\[
\Delta G_{ad} = E_{ad} + \Delta ZPE + \Delta U + RT - T\Delta S
\]
where $E_{ad}$ is the total energies from VASP calculations. The thermodynamic corrections of the gaseous species were calculated using the Gaussian 03 with ideal gas approximation.

In this work, the free energies of adsorption are calculated as follows:

$$G_{ad} = G_{tot} - (G_{surface} + G_g)$$

where $G_{ad}$ is the free energy of adsorption, $G_{tot}$ is the free energy of the system after adsorption, $G_{surface}$ is the free energy of the clean surface and $G_g$ is the free energy of the gas molecule. The transition states (TS) were searched using the constrained minimization technique and the quasi-Newton algorithm.\textsuperscript{6-9} The transition states were verified by two key facts: (i) all forces on atoms have been optimized to be less than 0.05 eV/Å; (ii) the total energy is a maximum along the reaction coordinate but a minimum with respect to all other degrees of freedom.

S1.2 Solvent Co-catalyzed Mechanism Calculations

The solvent co-catalyzed mechanism is investigated with AIMD, in which explicit solvent molecules on the solid surface was used for an accurate description of the processes associated with the solid–liquid environment.\textsuperscript{10} In the liquid phase calculations, the methanol solvent consisted of 20 methanol molecules placed randomly above the MnO$_2$ surface to explicitly simulate the methanol/MnO$_2$ interface with an approximate density of an approximate fixed density of 0.792 kg m$^{-3}$. The AIMD was performed using VASP in forms of constrained MD. The Nosé-Hoover thermostat was used to control the temperature in the MD simulations, and the free energy is the Helmholtz free energy corresponding to the NVT ensemble.\textsuperscript{11} The artificial energy added on reaction coordinates was based on Gaussian hills as:

$$V = h \times \exp \left( -\frac{|x_i - x_0|^2}{2w^2} \right)$$

where $x_i$ is reaction coordinate $i$ of each MD step and $x_0$ is the reaction coordinate where the artificial bias energy is set. The $h$ and $w$ are the height and width of Gaussian peak. The artificial potential well is set with a height of -6.0 eV and a width of 0.5 Å in this work. The free energy profiles were calculated using umbrella sampling, where the restricted coordinate was the distance between the two atoms for the respective bond formation step. The pathway was sampled between different $R$–$R$ coordinate distances, of 0.1 Å intervals, and each sampling was carried out for at least 10 ps.
S2 Optimization of the Birnessite Surface

Birnessite is an octahedrally layered manganese oxide naturally found, which possesses oxygen vacancies. The spaces between the layers can be synthesized to possess a number of different metals which commonly include K, Na and Ca. In our system, K is chosen as the metal between the layers. Our optimized structure for the birnessite catalytic surface is shown in Figure S1. The model is similar to the structure modelled from the study by Gaillot et al. The distance between the layers in our model is 6.43 Å, which is similar to those obtained from their experiments (6.39 Å). To probe the mechanism for hydrogenations of acetaldehyde, a $6 \times 4 \times 2$-unit cell with a 15 Å vacuum space was created to prevent spurious interactions between periodically repeated supercells (Figure S1c). This is the same supercell used in the liquid phase simulations; however, the vacuum layer has been filled with methanol to accurately depict solvent effects.

**Figure S1** The structure of the birnessite model – (a) the optimized lattice of OL and (b) depicting the layered surface with general formula KMn$_2$O$_4$. The red, grey, and purple balls represent oxygen, manganese, and potassium respectively. (c) and (d) are the structures of the optimised $6 \times 4 \times 2$-unit cell with 15 Å vacuum space from side and top views.
S3 Initial Structure

The first point to note is that without the formation of an oxygen vacancy, no adsorption of hydrogen or acetaldehyde can occur on the flat surface. In effect, the surface can be interpreted as being inert as the reactant molecules just hover above the surface with no chemistry taking place. However, birnessite by nature also has many edge surfaces, which can potentially offer a metal adsorption site. We tested the adsorption of acetaldehyde and H$_2$ on the edge surface, and the adsorption structures are shown in Figure S2 and adsorption energies are listed in Table S1. An exposed Mn was tested as an adsorption site on the edge surface. However, both reactants have very weak adsorption, which is similar to the flat surface.

![Figure S2](image)

**Figure S2.** (a) The structure of O vacancy-free edge surface; the green circle represents the favorable adsorption site. The structures for adsorptions of (b) H$_2$ and (c) C$_2$H$_4$O.

**Table S1.** Adsorption energies (eV) of H$_2$ and C$_2$H$_4$O on the surface with edges.

|                | H$_2$ | C$_2$H$_4$O |
|----------------|-------|-------------|
| Adsorption Energy (eV) | 0.28  | -0.19       |

Therefore, this work focuses solely on the flat surface for the purpose of generalization. When oxygen vacancies are formed on the flat surface, which is a common state of the catalyst, both the hydrogen molecule and acetaldehyde can adsorb to the surface. The hydrogen molecule has an adsorption energy of -0.67 eV and the acetaldehyde molecule possesses an adsorption energy of -2.22 eV. The adsorption strength of the aldehyde is large, which can be rationalized by the fact that the oxygen bonds to three Mn centers. This offers a significant level of bonding with the d orbitals of the metal, resulting in strong interactions of their electron clouds and thus
a strong bond. The initial structure is shown in Figure S3, where the hydrogen molecule and acetaldehyde adsorb on two oxygen vacancies in close proximity to each other.

![Figure S3](image)

**Figure S3.** Illustration of (a) the positions of the oxygen vacancies and (b) the initial structure, showing the adsorption of H$_2$ and C$_2$H$_4$O on those oxygen vacancies. The red, purple, grey and white balls depict O, Mn, C and H atoms, respectively.

To test the thickness of the slab model, we also built a three layers model for birnessite with the top two layers relaxed and the bottom layer fixed. The adsorptions structures are shown in the Figure S4, and the adsorptions energies are listed in Table S2.
Figure S4. The adsorption structures of H\(_2\) and C\(_2\)H\(_4\)O on a three-layer birnessite surface from (a), (b) top views and (c), (d) side views.

Table S2. Comparison between the adsorption energies (eV) of H\(_2\) and C\(_2\)H\(_4\)O on the 3-layer birnessite model and the 2-layer model.

|                | 2-layer model | 3-layer model |
|----------------|---------------|---------------|
| H\(_2\)        | -0.67         | -0.59         |
| C\(_2\)H\(_4\)O| -2.22         | -2.09         |

As shown in the table S2, the adsorptions energies calculated from the 3-layer model are very close to the results obtained from the 2-layer model; the errors are much smaller than the energy differences to distinguish the different mechanisms. Therefore, a two-layer model is sufficient for the calculations.
S4 Investigation of the non-Horiuti-Polanyi Mechanism

The non-Horiuti-Polanyi mechanism was investigated as the hydrogenation proceeds through molecular hydrogen, which starts right after the initial structure. The reaction mechanism is shown in Figures S5. The first step in this mechanism after adsorption of the reactants is the attack of one H from molecular hydrogen to either the C or O of the unsaturated C=O. The results from DFT calculations show unequivocally that attack of the C of C=O is heavily favored, shown in Figure 2a of the main text. The barrier for attack of C is 0.31 eV compared to 0.83 eV for O, which is expected as the carbon is activated from the adsorption of the O to the surface. The bonding of the aldehyde to the surface is large which will also increase the reaction barrier for O hydrogenation. Additionally, when we optimized the structure after the hydrogenation of O, we found that the H goes back to the surface forming a hydroxyl group as shown in IMS. This suggests that hydrogenating the O first forms an unstable structure and confirms that the first point of hydrogenation is the C. The second step involves the addition of the second H which is now on the oxygen vacancy. The barrier for the addition of the second H to the O atom is huge with a value of 2.13 eV. The addition of the first hydrogen results in the three Mn-H bonds shortening from 1.95, 1.93, and 1.75Å to 1.84, 1.83, and 1.73Å, respectively. This means the H is more strongly and tightly bonded to the catalytic surface and thus the removal from the vacancy is markedly more difficult. The H addition to the strongly bonded O atom of the aldehyde with the surface is also a prohibiting factor, explaining why this secondary hydrogenation step is so difficult.
Figure S5. The reaction mechanisms for the non-Horiuti-Polanyi hydrogen on the surface using molecular hydrogen from (a) side views and (b) top views where IS, IMS, TS and FS stand for the initial state, intermediate state, transition state and final state, respectively.

S4 Investigation of the Horiuti-Polanyi Mechanism

The Horiuti-Polanyi mechanism was then investigated. The first step after H₂ and acetaldehyde adsorption on the oxygen vacancies in the Horiuti-Polanyi mechanism is the dissociation of H₂ on the surface. The dissociation of H₂ on birnessite results in one H on the oxygen vacancy and the other H forming a hydroxyl group (OH) on the surface. This can occur relatively easy with a barrier of 0.39 eV with the reaction mechanism shown in Figures S6.
The reaction mechanism for the dissociation of hydrogen on the surface from (a) side views and (b) top views.

The dissociation of H₂ into Mn-H and Mn-OH leaves two possible reaction pathways for the reaction to proceed. The reaction mechanisms of the two pathways are shown in Figures S7. The hydrogen from Mn-H can react first with the unsaturated the C of C=O of acetaldehyde followed by subsequent hydrogenation from the Mn-OH. Alternatively, the Mn-OH can react first, followed by hydrogenation from the Mn-H. In this case, only the C of the C=O are treated as the target due to the large reaction barriers of O attack, which will be discussed in the following section. The attack from the Mn-H to the C of the C=O was calculated to be favored over the attack from the hydrogen of Mn-OH by 0.18 eV: The reaction barrier is 0.65 eV from Mn-H compared to 0.83 eV from Mn-OH. The intermediate state (IMS) as a result of the attack from Mn-H was also calculated to be energetically more stable by 0.04 eV, although this value is relatively small. The second step of the hydrogenation shows the opposite result. The H addition from Mn-OH is more favorable than that from Mn-H by a considerable amount of energy (0.64 eV). Both barriers are large with effective barriers of 1.49 eV and 2.13 eV for Mn-OH and Mn-H, respectively, shown in Figure 2b of the main text.
**Figure S7.** The Horiuti-Polanyi mechanisms on the surface using hydrogen atom from (a) side views and (b) top views, where IS, IMS, TS and FS stand for the initial state, intermediate state, transition state and final state, respectively.

**S5 Investigation of the Coordination Mechanism**

The barriers of acetaldehyde hydrogenation when it is adsorbed on the surface in the Langmuir-Hinshelwood style mechanisms are large, as reported above and also in the main text. To overcome this problem, we decided to have the acetaldehyde coordinated to the surface instead of binding to the surface via a Eley-Rideal style mechanism. The first step in this approach is to force the hydrogen molecule to dissociate on the surface and create two hydroxyl groups whereby the acetaldehyde molecule can coordinate via hydrogen bonding to C=O bond. The acetaldehyde molecule has a coordination strength of -1.15 eV with the surface hydroxyl which is significantly lower than the -2.22 eV when directly bonded to the surface. The next step is the hydrogenation of the C=O of acetaldehyde by the hydroxyl group. Two pathways were
considered, the first starting with hydrogenation of the O of C=O, the other starts with the C. The hydrogenation barrier of the O by the hydroxyl group with which the molecule is coordinated is 0.27 eV. The primary problem in the investigations seen prior was the hydrogenation of the O, which is now possible when the molecule is not strongly adsorbed to the surface. However, the hydrogenation of the C is still very large, 1.52 eV. When we tested the second possible reaction pathway of attacking the C from C=O from the H from the hydroxyl group that the molecule is not coordinated, an interesting result was observed. This step resulted in the O of the C=O picking up the other H from the other hydroxyl group to which it was coordinated before the transition state was reached. This means that the hydrogenation reaction occurred in the same way as the first reaction pathway due to the small reaction barrier of hydrogenation of the O. This mechanism also gave the lowest barrier so far and is a mechanism that can be developed on. The high barrier does indicate, however, that this is not the mechanism for the reaction and that another mechanism is needed, where the hydrogen source is not strongly adsorbed to the surface.

S6 Investigation of the Solvent Co-catalyzed Mechanism by AIMD and Umbrella Sampling

First, to test whether a methanol molecule is more likely to adsorb than an acetaldehyde molecule a simple MD simulation was conducted. A methanol molecule and an acetaldehyde molecule were placed equidistant away from an oxygen vacancy and the system was allowed to optimize. The system was then completely optimized until all forces were below 0.05 eV / Å to act as a starting point for MD simulations. The optimized structure was then allowed to thermally equilibrate at 300 K for a minimum of 50 ps. The rest of the system was filled with methanol solvent to the correct density and with a molecular hydrogen in the liquid phase (see Figure 3b in the main text). The system was then optimized until the forces were under 0.05 eV and then an MD simulation was run for 50 ps at 300 K to allow the system to thermally equilibrate. The system is shown in Figure S8 below which is the system prior to constrained MD calculations.
Figure S8. The starting system for the hydrogenation of acetaldehyde in methanol solvent by molecular hydrogen.

From the MD simulations, the hydrogen molecule was observed to reside close to the surface and parallel to the C=O bond of the aldehyde. The acetaldehyde prefers to bond with the hydroxyl group in an upright position due to the presence of the methoxy group on the surface. This orientation reduces the steric strain on the system. To verify whether the explicit solvent model is sufficient to accurately describe the solvent environment, we also tested a larger system. A model which quadruple the size of the original model was built for comparison, as shown in Figure S9a and b. A 20 ps MD simulation was performed and the density results are shown in Figure S9c.
Figure S9. The side (a) and top (b) views of the unit cell with 80 methanol molecules to represent the solvent. (c) Average atomic density profile of methanol from the MD simulation of explicit solvent model. The black line indicates the average atomic density, grey dashed lines indicate the min/max density flux, and the red line indicates the density of standard methanol solvent (792 kg/m3).

By comparing the solvent part of Figure 3b in the main text and Figure S9c, we can see that the larger model possesses a similar density profile as the original one, indicating that the original system is sufficient. The original model is then used as the starting point for our umbrella sampling calculations to obtain free energies, where the hydrogen molecule was forced to react with the C and O of the acetaldehyde carbonyl bond. The free energy barriers of H\textsubscript{2} attacking the C of the C=O and the O of the C=O were calculated using Umbrella Sampling. It is worth noting that the umbrella sampling calculations are currently the state-of-the-art approach to obtain free energies in heterogeneous catalysis\textsuperscript{,10,13} in which the free energies can be accurately computed directly in contrast to the traditional correction method.
An umbrella sampling with the weighted histogram analysis method (WHAM), an approach used in our group previously,\textsuperscript{10,13–15} was conducted to analyze the free energy for the attack of the C and O of acetaldehyde. In the umbrella sampling simulation for the H\textsubscript{2} attacking C of the C=O, it was studied by the coordinate of the distance between one of the H atoms and the C of the C=O from 3.4 to 1.1 Å. A series of biased MD simulations were performed by the step of 0.1 Å of distance. The same calculations were performed for the H atom attacked the O of the C=O with distances between 3.4 to 1.1 Å. The WHAM code of Grossfield\textsuperscript{16} was used and the Gaussian peak model mentioned in S1.2 was chosen for constraints.\textsuperscript{17} To confirm the time scale of the AIMD simulations is sufficient, a series of tests were carried out using different time scales, listed in Table S3. We first performed the C and O attack using a time scale of 5 ps per window. We then tested the O attack with a time scale of 10 ps per window. The umbrella sampling analysis of the free energy barrier was calculated as 1.29 eV in the 10 ps test which is very close to the one obtained previously with a 5 ps window (1.25 eV). To provide further confirmation, we tested the C attack with a time scale of 20 ps per window. The umbrella sampling analysis of the free energy barrier was calculated as 0.92 eV which is slightly higher than the one obtained previously with a 5 ps window. It can be seen that the time scale of MD simulation is sufficient to obtain correct chemistry.

\textbf{Table S3.} Comparison between free energy barriers obtained by umbrella sampling analysis for the C/O attacks in different time scales.

|          | 5 ps/window (eV) | Extended to 10 ps/window (eV) | Extended to 20 ps/window (eV) |
|----------|-----------------|-------------------------------|-------------------------------|
| O-Attack | 1.25 eV         | 1.29 eV                       |                               |
| C-Attack | 0.83 eV         |                               | 0.92 eV                       |

The free energy results reported in the main text are the ones obtained by the extended MD simulation, the 10 ps per window MD simulation for the O attack and the 20 ps per window MD simulation for the C attack. The results of the free energies and error analysis of both umbrella samplings are listed in Table S4 and S5.

\textbf{Table S4.} The free energies and standard errors from the AIMD with umbrella sampling of the C-attack.

| Reaction Coordinates R\textsubscript{H-O} (Å) | Free Energy (eV) | Standard Error (eV) |
|---------------------------------------------|-----------------|--------------------|
| 1.1                                         | 0.802           | 0.00039            |
| 1.2                                         | 0.661           | 0.00059            |
| Reaction Coordinates $R_{H-O}$ (Å) | Free Energy (eV) | Standard Error (eV) |
|-----------------------------------|------------------|---------------------|
| 1.1                               | 0.646            | 0                   |
| 1.2                               | 1.221            | 0.00185             |
| 1.3                               | 1.294            | 0.00186             |
| 1.4                               | 1.259            | 0.00170             |
| 1.5                               | 1.062            | 0.00153             |
| 1.6                               | 0.924            | 0.00283             |
| 1.7                               | 0.695            | 0.00313             |

Table S5. The free energies and standard errors from the AIMD with umbrella sampling of the O-attack.
In order to further understand the solvent co-catalyzed mechanism, we hypothesized an equivalent gas-phase mechanism for comparison. The nudged elastic band (NEB) method\textsuperscript{18} was used to search for the transition state, starting from the structure shown in Figure S10. The free energies of the system were calculated as follows:

\[
G_{total} = E_{total} + G_{gas}^{\text{correction}} + G_{surface}^{\text{correction}}
\]

where \(G_{total}\) represents the free energy of the system, \(E_{total}\) is the total energy obtained from static DFT calculation, \(G_{gas}^{\text{correction}}\) represents the free energy correction of all the gas-phase molecules, and \(G_{surface}^{\text{correction}}\) is the free energy correction of the surface. Some key structures of the gas-phase pathway at 300 K are shown in Figure S10.
Figure S10. The energy profile and the key structures of the gas-phase mechanism where the pathway is similar to that of the favored mechanism (Figure 4 in the main text) except the explicit solvent molecules being removed. To distinguish different H sources, the H atoms from H₂ are highlighted by light blue. IS, TS, and FS stand for the initial, transition, and final states, respectively.

The barrier calculated is 1.21 eV which is considerably higher than the barrier calculated in the presence of the solvent (0.92 eV). If the rate constants of both gas-phase and liquid-phase reactions are analyzed by the Arrhenius equation, we find that the rate constant of the liquid-phase reaction is more than 5 orders of magnitude larger than that of the gas-phase reaction at the reaction temperature. Unlike the liquid-phase simulations, in which H₂ stays in the interface region between the liquid and the surface during long MD simulations, the H₂ concentration in the newly probed mechanism will be significantly lower since it moves freely in the gas phase. The reaction rate advantage of the liquid-phase reaction will be expanded even more with this difference in H₂ concentration. Therefore, the gas-phase mechanism is not favored.

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