



Cite this: *React. Chem. Eng.*, 2025, 10, 1244

## Hydride-mediated chemoselective C–H bond formation during benzoic acid hydrodeoxygenation on anatase TiO<sub>2</sub><sup>†</sup>

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The chemoselective hydrogenation of benzoic acid to aromatic products such as benzaldehyde, benzyl alcohol, toluene, and benzene is studied on anatase TiO<sub>2</sub> (001) using density functional theory (DFT) and microkinetic modeling (MKM). Oxygen vacancy (O<sub>vac</sub>) sites are more active for benzoic acid hydrogenation than fully oxidized surface regions, with a nearly 2.5 eV lower energy for the first C–H bond formation reaction to occur near O<sub>vac</sub>. This favorable C–H bond formation mechanism on anatase TiO<sub>2</sub> occurs between hydrides (H<sup>−</sup>) and monoanionic intermediates coadsorbed in O<sub>vac</sub>. A steady-state microkinetic model is constructed using computed reaction energies and activation barriers to determine rates of product formation at different reaction temperatures. Product selectivities differ in distinct temperature ranges, caused by competition among reaction and product desorption steps. Sensitivity analysis shows which elementary steps significantly affect the overall benzoic acid hydrogenation activity and selectivity.

Received 18th November 2024,  
 Accepted 3rd March 2025

DOI: 10.1039/d4re00561a

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### 1. Introduction

The production of aromatic products such as benzaldehyde, benzyl alcohol, toluene, and benzene<sup>1–3</sup> has been of interest due to their versatility as commodity chemicals and intermediates in chemical and pharmaceutical industries.<sup>4</sup> The chemoselective hydrogenation of benzoic acid has previously been identified as an attractive route for the formation of these aromatic products.<sup>1,2,5,6</sup> Benzoic acid is a relatively inexpensive feedstock that can be sourced from a variety of waste products. For example, polyethylene terephthalate (PET) plastic waste pyrolysis produced benzoic acid as the major product.<sup>7,8</sup> Thus, finding methods to catalytically upgrade benzoic acid to value-added products could make diverting PET plastic waste from landfills economically more feasible.

Selectivity is a challenging issue for aromatic carboxylic acid hydrogenation,<sup>9</sup> since hydrogenating the aromatic ring is typically easier than preserving its aromaticity and exclusively hydrogenating the carboxyl group.<sup>1,6,10,11</sup> Although some studies have demonstrated promising results in

achieving aromatic product selectivity, there remains considerable variation in both the distribution of products obtained and the proposed reaction mechanisms.<sup>2,5,12,13</sup> In principle, benzoic acid hydrogenation can produce aromatic products such as benzaldehyde, benzyl alcohol, benzene, and toluene (Fig. 1).<sup>1</sup> Notably, the carbon of the carboxyl group undergoes several C–H bond formation steps upon the consecutive hydrogenation of benzoic acid towards toluene. Meanwhile, benzene can be produced through the decarboxylation of benzoic acid<sup>12,14</sup> or the decarbonylation of benzaldehyde.<sup>15,16</sup> Benzene production *via* the demethylation of toluene appears unlikely as only CO and CO<sub>2</sub> (*i.e.*, no CH<sub>4</sub>) are detected under relevant conditions.<sup>17,18</sup> Among the possible aromatic products of benzoic acid, hydrogenated products such as toluene and benzyl alcohol are often preferred over benzaldehyde due to their value-added demand as solvents and ester precursors.<sup>14,19–21</sup>

The development of a superior catalyst for the selective hydrogenation of benzoic acid, capable of achieving high selectivity for specific aromatic products, remains an active area of research.<sup>6,9</sup> Numerous studies focused on ring hydrogenation for cyclohexanecarboxylic acid production.<sup>22–26</sup> While some studies have reported supported metals such as Au<sup>1,16,27</sup> and Pt<sup>2</sup> to be selective for aromatic products, the specific role of oxide catalysts or supports in benzoic acid hydrogenation remains unclear. Early studies have reported high yields and selectivity for benzaldehyde on ZrO<sub>2</sub> (ref. 5 and 6) and CeO<sub>2</sub>,<sup>28</sup> albeit at higher temperatures than on extended metal clusters. For example, benzoic acid hydrogenation on Au/CeO<sub>2</sub> was reported to occur at 573 K,<sup>1</sup>

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<sup>†</sup> Electronic supplementary information (ESI) available: Computational methods and details, alternative mechanisms of product formation, additional geometric details and configurations of reaction intermediates, overall reaction energy diagram, kinetic model parameters and differential equations, surface coverages, and detailed rate analysis. See DOI: <https://doi.org/10.1039/d4re00561a>

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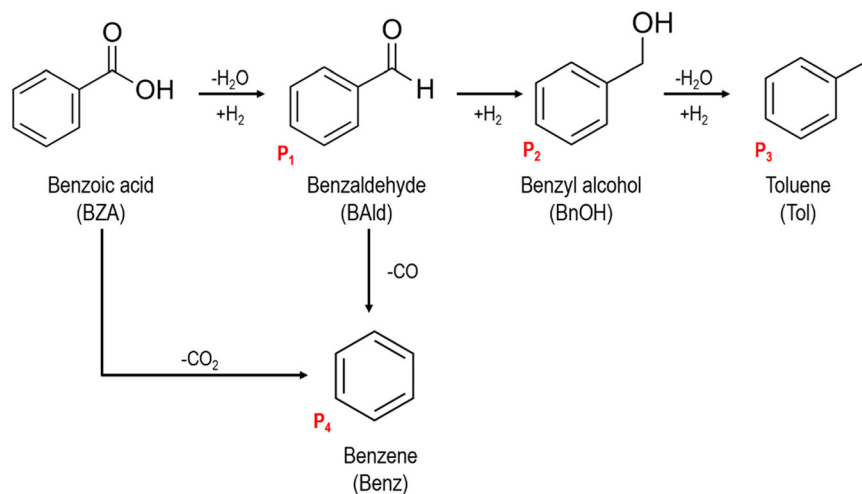


Fig. 1 Reaction scheme for the chemoselective hydrogenation of benzoic acid to aromatic products.

while activity on  $CeO_2$  occurs between 523–723 K.<sup>28</sup> The only study of benzoic acid hydrogenation on  $TiO_2$  reported lower selectivity for benzaldehyde and higher selectivity for toluene and benzene (*i.e.*, relative to  $HfO_2$  and  $ZrO_2$ ).<sup>6</sup> Ponec *et al.* hypothesized from their experiments on various metal oxides that the M–O bond strength and, by extension, the concentration of surface oxygen vacancy ( $O_{vac}$ ) sites dictates the selectivity for benzaldehyde.<sup>6,9,28</sup> The same authors suggested mechanisms such as a reverse Mars and van Krevelen or radical-like benzoate decomposition as responsible for benzaldehyde formation.<sup>9,28,29</sup> To date, no *ab initio* studies have been published to provide atomistic confirmation of elementary reaction mechanisms or selectivity determining steps in benzoic acid hydrodeoxygenation (HDO) on metal oxides.

The search for highly selective catalysts for the chemoselective hydrogenation of complex aromatics is not exclusive to benzoic acid hydrogenation. Single-atom catalysts (SACs), with metals atomically dispersed on a support,<sup>30,31</sup> have emerged as remarkably selective catalysts for similar reactions. For example, Liu *et al.* reported highly active and selective Ag SACs on anatase  $TiO_2$  for phenolic products from guaiacol, a biomass-derived aromatic (*i.e.*, aromatic products preferred over ring hydrogenation).<sup>32</sup> Both experimental and DFT studies confirm that the Ag single atoms serve as sites for  $H_2$  activation and a source of continuous hydrogen spillover to the  $TiO_2$  support.<sup>32–34</sup> Since single atom catalysts have the metal atomically dispersed on the surface at extremely low coverages<sup>35,36</sup> and because Ag is typically not active for hydrogenation,<sup>32</sup> the vast majority of hydrogenation reactions, such as C–H bond formation, is expected to occur on the  $TiO_2$  surface (*i.e.*, whereas the metal mainly acts as a source of spillover H atoms).

Since hydrogenation conditions over metal oxides require temperatures above 523 K,<sup>28</sup> the presence of  $O_{vac}$  is expected on the oxide surface.<sup>37,38</sup> Nuclear magnetic resonance (NMR) results<sup>39</sup> as well as our previous work<sup>33</sup> on anatase  $TiO_2$  have identified hydrides in  $O_{vac}$  as stable species of spillover H

atoms when the surface is exposed to high temperature reducing conditions. Thus, in this paper, we use DFT and MKM to achieve two goals: 1) determine the mechanisms and selectivity of benzoic acid hydrodeoxygenation on anatase  $TiO_2$ , and 2) examine the roles and effects that  $O_{vac}$ -adsorbed hydrides have in the hydrodeoxygenation reaction in general and the C–H bond formation steps in particular.

## 2. Methods

### 2.1. Development of surface models

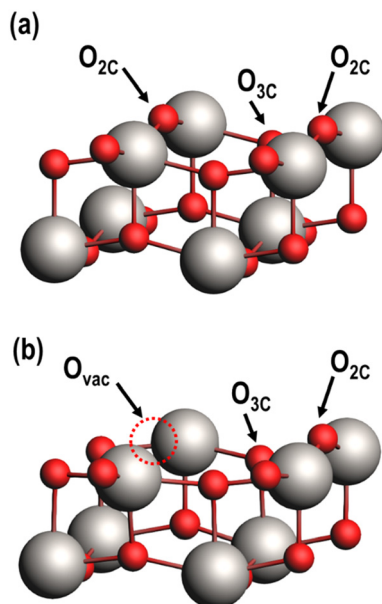
The (001) facet of anatase  $TiO_2$ , a low index facet of anatase considered to be the most active for catalytic reactions,<sup>40–42</sup> was used for this study. Periodic  $2 \times 2$  supercells of (001) anatase were constructed with a vacuum region of 15 Å above the slab to minimize periodic dipole interactions normal to the surface. The slab is two layers thick, with each layer defined as the minimum depth of atoms to achieve  $Ti_nO_{2n}$  stoichiometry in the  $2 \times 2$  supercell; each layer is comprised of three atomic sublayers (*i.e.*, six atomic layers in total to form a  $Ti_{24}O_{48}$  unit cell). The three uppermost atomic layers are allowed to freely relax during geometric optimizations, while the bottom three layers are fixed in position to model the bulk anatase support (Fig. S1†). Atomic figures shown in this publication were constructed using the Amsterdam modeling suite (AMS).<sup>43</sup>

Surface oxygen atoms are characterized based on their local coordination, with oxygens coordinated to two and three Ti atoms referred to as  $O_{2C}$  and  $O_{3C}$ , respectively (Fig. 2a).  $O_{vac}$  readily form on the surface as a result of  $TiO_2$  reduction (*i.e.*, two spillover H atoms combine with a surface O to desorb as  $H_2O$  and leave an  $O_{vac}$ ).<sup>44,45</sup> Previous studies have established that bridging  $O_{2C}$  atoms require the least amount of energy to form a vacancy,<sup>33,46</sup> so models of the reduced  $TiO_2$  (001) surface have an  $O_{2C}$  vacant (Fig. 2b).

### 2.2. Electronic structure methods

DFT was implemented through the Vienna *ab initio* simulation package (VASP)<sup>47</sup> using the Perdew–Burke–





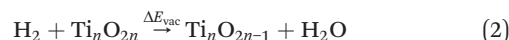
**Fig. 2** The anatase  $\text{TiO}_2$  (001) surface with (a) the fully oxidized surface having one pair each of  $\text{O}_{2\text{C}}$  and  $\text{O}_{3\text{C}}$ , and (b) a reduced surface with an  $\text{O}_{2\text{C}}$  substituted with an  $\text{O}_{\text{vac}}$ . Only the two uppermost atomic layers are shown for clarity. Ti (gray), O (red), and an  $\text{O}_{\text{vac}}$  (dashed circle) are depicted.

Ernzerhof (PBE) exchange correlation functional.<sup>48</sup> The projector augmented-wave (PAW) method was used to take into account core–valence interactions<sup>49</sup> and PBE + D3 was used to correct for dispersion interactions.<sup>50,51</sup> The self-interaction error from strongly correlated d-orbital electrons on Ti requires the use of DFT+U corrections on Ti.<sup>52</sup> The Hubbard's  $U$  parameter was set to 3 eV, as it was confirmed to give reasonable results for the energy of reduction of  $\text{TiO}_2$  to  $\text{Ti}_2\text{O}_3$  and was proposed for computing redox cycles on  $\text{TiO}_2$  by Hu and Metiu.<sup>53</sup> During geometric optimizations, iterative calculations were considered converged when the forces on atoms reached less than  $0.05 \text{ eV } \text{\AA}^{-1}$ . The self-consistent field tolerance was set to  $10^{-5} \text{ eV}$ . All calculations were spin-polarized. The Monkhorst–Pack  $k$ -point mesh of  $3 \times 3 \times 1$  and a plane-wave basis set cutoff energy of 450 eV were used.<sup>54,55</sup> Valence electrons considered for each atom type were Ti ( $3s^2 3p^6 4s^1 3d^3$ ), O ( $2s^2 2p^4$ ), C ( $2s^2 2p^2$ ), and H ( $1s^1$ ). Transition state searches were performed using the climbing image nudged elastic band method (CI-NEB), with the search considered converged when the transition state has a tangent force less than  $0.05 \text{ eV } \text{\AA}^{-1}$  and one imaginary vibrational frequency.

Adsorption energy of an adsorbate to the  $\text{TiO}_2$  surface ( $\Delta E_{\text{ads}}$ ) was calculated as:

$$\Delta E_{\text{ads}} = E_{\text{adsorbate\_on\_surface}} - E_{\text{adsorbate}} - E_{\text{bare\_surface}} \quad (1)$$

Here,  $E_{\text{adsorbate}}$  is the gas phase adsorbate energy. Desorption energies are calculated from the adsorption energies as  $\Delta E_{\text{des}} = -\Delta E_{\text{ads}}$ .  $\text{O}_{\text{vac}}$  formation energies ( $\Delta E_{\text{vac}}$ ) were calculated with respect to gas phase  $\text{H}_2$  and  $\text{H}_2\text{O}$  (eqn (2)).



Co-adsorption effects of two adsorbates, A and B, were quantified using a co-adsorption energy ( $\Delta E_{\text{CoAds}}$ ) respective to A and B co-adsorbed on the same  $\text{O}_{\text{vac}}$  site and the two adsorbates bound separately to  $\text{O}_{\text{vac}}$  site on individual reduced  $\text{TiO}_2$  unit cells ( $\text{Ti}_n\text{O}_{2n-1}$ ) (eqn (3)):



Zero-point vibrational energies (ZPVE) for all gas phase molecules and adsorbates were included to correct for the energy contribution of harmonic vibrational frequencies at 0 K.

### 2.3. Kinetic model development

A dual site microkinetic model (MKM) was constructed to predict the hydrogenation performance of anatase  $\text{TiO}_2$  (001) at reaction conditions. Reduced  $\text{TiO}_2$  sites were used to facilitate the C–H bond formation reactions occurring at  $\text{O}_{\text{vac}}$  (\*), while spillover H atoms are sourced from fully oxidized regions away from the C–H bond formation sites (\*\*). When H atoms are needed for each C–H bond formation step, the spillover H atoms are assumed to be continuously sourced from (\*\*). The coordinates of all surface intermediates and transition states included in our MKM are provided in the Appendix within the ESI†

A gas-phase reference adjustment is made for DFT adsorption and desorption energies in the MKM to match the overall thermodynamics to the NIST gas-phase thermodynamic values (see eqn (S1), Table S1†).<sup>56,57</sup> Entropy changes corresponding to adsorption or desorption of gas phase species were calculated using correlations available in the literature for standard gas phase absolute entropies as a function of temperature<sup>58,59</sup> and approximations of their entropies as adsorbed species developed by Campbell *et al.* (eqn (4)).<sup>60</sup> More specifically,

$$S_{\text{ads}}^0(T) = 0.70S_{\text{gas}}^0(T) - 3.3R \quad (4)$$

where  $S_{\text{ads}}^0(T)$  is entropy of the adsorbed species at temperature  $T$ , and  $S_{\text{ads}}^0(T)$  is gas-phase entropy at temperature  $T$  obtained from the NIST database. A comparison of adsorbed species entropies using different approaches (immobile, mobile and quasi-harmonic approximations)<sup>61</sup> for the main products including benzaldehyde, toluene and benzene is included in Fig. S2†. Additionally, the entropy of the desorption transition state at temperature  $T$  ( $S_{\text{TS,des}}^0(T)$ ) was calculated as:

$$S_{\text{TS,des}}^0(T) = S_{\text{ads}}^0(T)/0.68 \quad (5)$$

Adsorption and desorption entropies are then defined as  $\Delta S_{\text{ads}}^0 = S_{\text{ads}}^0 - S_{\text{gas}}^0$  and  $\Delta S_{\text{des}}^0 = S_{\text{TS,des}}^0 - S_{\text{ads}}^0$ , respectively. Using eqn (4)



may slightly overestimate the entropy loss of adsorbates that can dissociate such as H<sub>2</sub>. Instead,  $\Delta S_{\text{ads}}^0$  of H<sub>2</sub> dissociative adsorption is approximated as  $-47.7 \text{ J mol}^{-1} \text{ K}^{-1}$ , as reported by Vannice *et al.*<sup>62</sup> Entropy changes for reactions between surface intermediates are assumed to be negligible.

Equilibrium constants were calculated for each elementary step  $i$  using standard free energy changes ( $\Delta G^0$ ) that combine the re-referenced DFT energetics with the aforementioned approximations for the entropy changes ( $\Delta S^0$ ):<sup>63,64</sup>

$$K_{\text{eq},i} = \exp\left(\frac{-\Delta G_i^0}{RT}\right) = \frac{k_i}{k_{-i}} \quad (6)$$

where  $T$  is the temperature, and  $R$  is the ideal gas constant. Reaction rate constants ( $k_i$  and  $k_{-i}$ ) were calculated using the Eyring equation with the attempt frequency from transition state theory as the pre-exponential factor:<sup>65,66</sup>

$$k_i = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_i^{0,\ddagger}}{RT}\right) \quad (7)$$

where  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant, and  $\Delta G^{0,\ddagger}$  is the standard free energy of activation as calculated from the re-referenced DFT energetics and the aforementioned approximations for the entropy changes ( $\Delta S^0$ ). For adsorption/desorption steps including the dissociative/associative adsorption/desorption of H<sub>2</sub>, the rate constant was defined for the desorption direction using eqn 7, while the adsorption rate constant was calculated from the desorption rate constant and the equilibrium constant (eqn (6)). For the elementary steps involving only surface intermediates, transition states were only found for those deemed kinetically relevant, such as those involving C–H bond formation during HDO,<sup>67,68</sup> hydrogen shifts and C–C bond breaking during decarboxylation or decarbonylation.<sup>69</sup> For the rest of those steps, eqn (7) was used to define the rate constant in the endothermic direction by replacing the free energy of activation with the reaction energy in that direction, with the rate constant in the exothermic direction ending up as  $k_B T/h$ .

To determine surface coverages and reaction rates, a set of ordinary differential equations is setup (see eqn (S3) in ESI†) and integrated with time until steady state is reached, namely:

$$\frac{d\theta_j}{dt} = \sum_i v_{ij} r_i = 0 \quad (8)$$

where  $v_{ij}$  is the stoichiometric coefficient of surface species  $j$  in reaction  $i$  and  $r_i$  is the net rate of reaction  $i$ . The relative selectivity of product  $p$  is referenced to the rates of production for all four products of interest (*i.e.*, benzaldehyde, benzyl alcohol, toluene, and benzene) (eqn (9)).<sup>63</sup>

$$\text{Sel}_p = \frac{r_p}{\sum_p r_p} \quad (9)$$

Sensitivity analysis of the product formation rates was performed with respect to individual kinetic rate constants

using the degree of rate control (eqn (10)),<sup>63,70,71</sup> with each reaction rate constant perturbed by 2% and the rate of reactant consumption (*i.e.*, benzoic acid) taken to be the rate of interest.

$$X_{\text{RC},i} = \left( \frac{\partial \ln r_{\text{BZA}}}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (10)$$

The partial equilibrium index (PEI) was calculated for each elementary reaction to gauge which steps are near equilibrium, thus not likely to be the rate determining step (eqn (11)).<sup>72,73</sup> A reaction step with a PEI between 0.45 and 0.55 is generally considered partially equilibrated.

$$\text{PEI}_i = \frac{r_i}{r_i + r_j} \quad (11)$$

### 3. Results and discussion

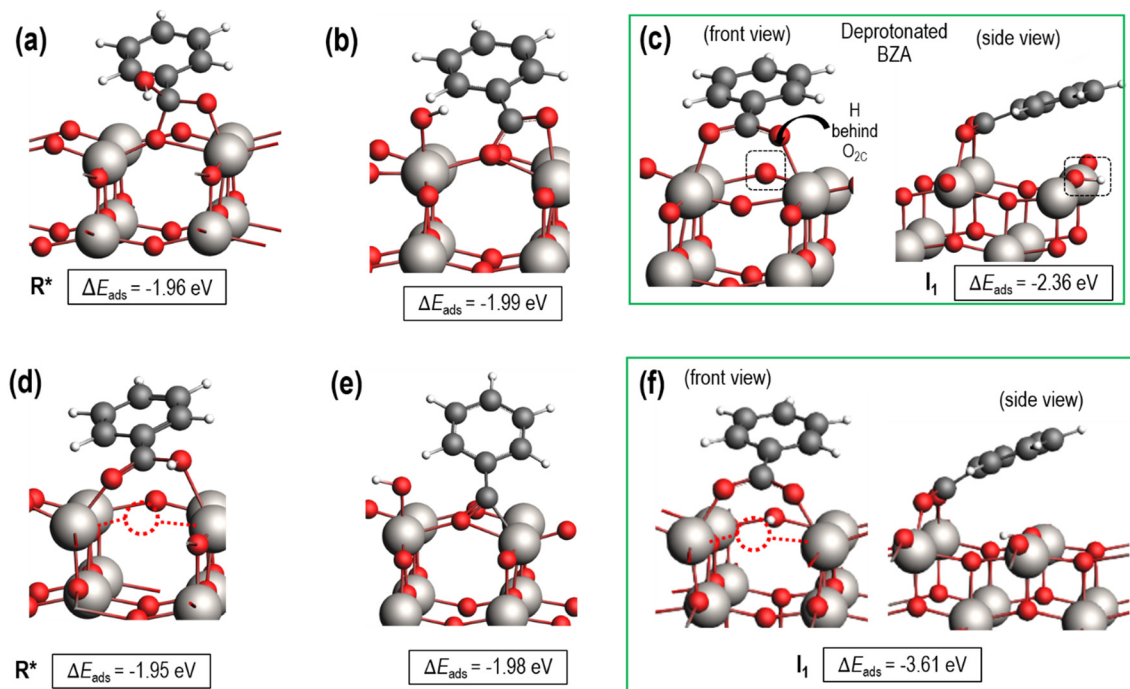
#### 3.1. Adsorption of benzoic acid on fully oxidized and reduced TiO<sub>2</sub>

Both fully oxidized and reduced sites on anatase (001) will be present at high temperature hydrogenation conditions. This is evidenced by H<sub>2</sub>O desorption and, by extension, O<sub>vac</sub> formation during temperature programmed reduction (TPR)<sup>6,32</sup> and the presence of reduced Ti states using resonant photoemission spectroscopy.<sup>74</sup> DFT results quantified an O<sub>vac</sub> formation energy of  $\Delta E_{\text{vac}} = 1.57 \text{ eV}$  on this (001) surface, while this energy decreases as low as  $\Delta E_{\text{vac}} = 1.03 \text{ eV}$  near Ag single atoms.<sup>33</sup> Thus, stable adsorption structures were determined for benzoic acid on both the fully oxidized and reduced (*i.e.*, with an O<sub>vac</sub>) surfaces of anatase (001) (Fig. 3).

Benzoic acid molecular adsorption is thermodynamically favorable on both the fully oxidized (Fig. 3a) and reduced (Fig. 3d) surfaces, with  $\Delta E_{\text{ads}}$  around  $-2 \text{ eV}$  for both. On the O<sub>vac</sub> surface, benzoic acid adsorbs into the vacancy with Ti–O bond formation between the O atoms of benzoic acid and each of the Ti atoms near the O<sub>vac</sub>. This favorable adsorption state is 0.6 eV more stable than with a single O atom from benzoic acid bound in approximately the O<sub>vac</sub> position (not shown). Dissociation of the hydroxyl group from benzoic acid is marginally more favorable on the fully oxidized (Fig. 3b) and reduced surfaces (Fig. 3e). However, dissociative adsorption of benzoic acid *via* deprotonation into an O<sub>vac</sub>-bound benzoate anion and a proton on an O<sub>2C</sub> was thermodynamically more favorable by 0.4 eV on the fully oxidized surface (Fig. 3c) and more than 1.5 eV on the reduced surface (Fig. 3f). These results agree well with studies which used infrared reflection-adsorption spectroscopy (IRRAS),<sup>75</sup> as well as scanning tunneling microscopy (STM) and low energy electron diffraction (LEED)<sup>76</sup> to confirm the spontaneous dissociative adsorption of benzoic acid to benzoate and hydroxyl groups on TiO<sub>2</sub>. The deprotonated adsorption structure is consistent with previous DFT studies of benzoic acid adsorption.<sup>77–79</sup> Furthermore, carboxylic acid







**Fig. 3** Benzoic acid adsorption on fully oxidized and reduced anatase  $\text{TiO}_2$  (001). Top row (a–c): Benzoic acid adsorbs on the fully oxidized surface either (a) molecularly, (b) dissociatively with the  $-\text{OH}$  group on a Ti atom, and (c) dissociatively by deprotonation. Bottom row (d–f): Benzoic acid adsorption on the reduced anatase  $\text{TiO}_2$  (001) surface with an  $\text{O}_{\text{vac}}$  of an  $\text{O}_{2\text{C}}$  site. Stable structures included benzoic acid (d) molecular adsorption, (e) dissociative adsorption with  $-\text{OH}$  on a Ti atom, and (f) dissociative adsorption by deprotonation.  $R^*$  and  $I_1$  labels in a), c), d), and f) are referenced in Fig. 4. Ti (gray), O (red), C (black), H (white), and an  $\text{O}_{\text{vac}}$  (dashed circle) are depicted.

deprotonation on anatase  $\text{TiO}_2$  is not only thermodynamically favorable but also essentially barrierless, with an experimental study reporting a barrier of around 0.05 eV for formic acid deprotonation on anatase (101) at 300 K.<sup>80</sup> Thus, further steps of hydrodeoxygenation are assumed to proceed from deprotonated, adsorbed benzoic acid on both the fully oxidized and reduced  $\text{TiO}_2$  surfaces.

### 3.2. Benzoic acid hydrogenation to benzaldehyde on fully oxidized $\text{TiO}_2$ (001)

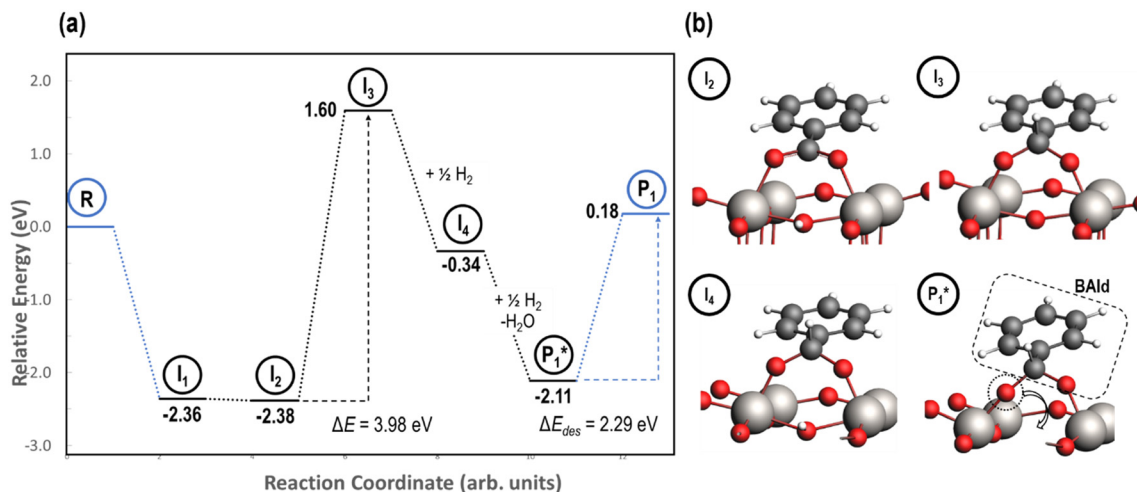
Stable structures were compiled along a plausible path of the first C–H bond formation of benzoic acid to benzaldehyde on the fully oxidized  $\text{TiO}_2$  (001) surface. These structures and their relative energies were used to build a reaction energy diagram (Fig. 4). Starting with gas phase benzoic acid and the bare  $\text{TiO}_2$  (001) surface, benzoic acid dissociatively adsorbs on the surface in its deprotonated form, as a benzoate anion and a  $\text{H}^+$  ( $I_1$ , Fig. 3c). The H atom then migrates to the support  $\text{O}_{2\text{C}}$  near to the benzoate anion ( $I_2$ );  $I_2$  is the most stable state compared to other structures of H adsorbed on atoms near the benzoate species. The first C–H bond formed ( $I_3$ ) by H migration from  $\text{O}_{2\text{C}}$  to the carboxyl C proceeds uphill in energy by 3.98 eV. To close the catalytic cycle, a series of elementary steps follows, where  $\text{O}_{\text{vac}}$  is formed on  $\text{O}_{2\text{C}}$  next to the deprotonated phenylmethanediol ( $I_3$ ), whose O atom refills the vacancy as a final step, producing benzaldehyde as a result of that step; the stepwise

addition of 2 H atoms and desorption of O as  $\text{H}_2\text{O}$  (*i.e.*,  $\text{I}_3 + 1/2\text{H}_2 \rightarrow \text{I}_4$  and subsequently  $\text{I}_4 + 1/2\text{H}_2 \rightarrow \text{P}_1^* + \text{H}_2\text{O}$ ) occur favorably. The final adsorbed state is essentially an oxidized precursor of benzaldehyde ( $\text{P}_1^*$ ). The desorption of benzaldehyde into the gas phase ( $\text{P}_1$ ) reforms the fully oxidized  $\text{TiO}_2$  surface and requires a reaction energy of 2.76 eV. Based on the reaction energy diagram of Fig. 4, *at least* 3.98 eV energy is required to form benzaldehyde from benzoic acid on the fully oxidized surface even without any kinetic barriers, indicating that this mechanism is too unfavorable to occur at relevant reaction temperatures.

### 3.3. Benzoic acid hydrogenation to benzaldehyde and decarboxylation to benzene on reduced $\text{TiO}_2$ (001)

The reaction energy profile of benzoic acid hydrogenation to benzaldehyde and decarboxylation to benzene on the reduced  $\text{TiO}_2$  (001) surface with an  $\text{O}_{\text{vac}}$  was determined (Fig. 5). The relative energies are referenced to gas phase benzoic acid and the reduced  $\text{TiO}_2$  (001) surface with an  $\text{O}_{\text{vac}}$ . Dissociative adsorption of benzoic acid into the benzoate anion (on the  $\text{O}_{\text{vac}}$ ) and  $\text{H}^+$  (on the  $\text{O}_{2\text{C}}$  opposite of the  $\text{O}_{\text{vac}}$ ,  $I_1$ , Fig. 3f) is enthalpically favorable by 3.6 eV. The proton adsorbed on  $\text{O}_{2\text{C}}$  then migrates into the  $\text{O}_{\text{vac}}$ , forming a hydride species ( $I_2$ ).<sup>33,39</sup> In effect, this state has two ( $-1$ ) anions co-adsorbed in an  $\text{O}_{\text{vac}}$ , benzoate and  $\text{H}^-$ . The migration of H into  $\text{O}_{\text{vac}}$  to form two anionic species ( $I_1 \rightarrow I_2$ ) proceeds uphill by 0.79 eV. The benzoate and hydride





**Fig. 4** Reaction energy diagram (a) with optimized intermediate structures (b) of benzoic acid hydrogenation to benzaldehyde on fully oxidized anatase TiO<sub>2</sub> (001). Stable intermediate I<sub>1</sub> corresponds to Fig. 3c. The energies of stable intermediates are referenced to gas phase benzoic acid and the fully oxidized TiO<sub>2</sub> (001) surface. Structures with gas phase molecules are circled in blue and adsorbed species in black. Only the uppermost atomic layer is shown for the sake of clarity. Ti (gray), O (red), C (black), and H (white) are depicted.

co-adsorption energy using eqn (3) is 0.58 eV, showing there is a repulsive interaction to placing two anionic ligands on the same O<sub>vac</sub> site. From intermediate I<sub>2</sub>, either C-H bond formation leading to benzaldehyde or decarboxylation leading to benzene can occur.

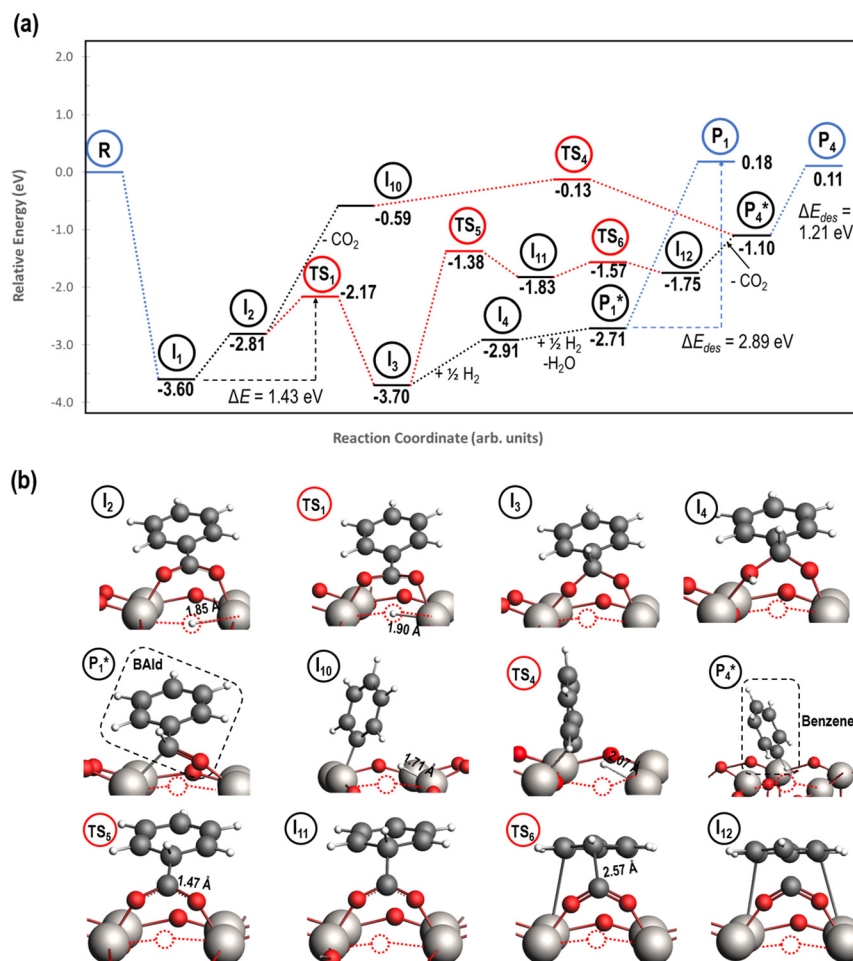
We first examine how intermediate I<sub>2</sub> may proceed to form benzaldehyde. The reaction between the hydride and benzoate in the vacancy results in a C-H bond formation (I<sub>2</sub> → I<sub>3</sub>), which proceeds downhill in reaction energy by 0.89 eV with a barrier of 0.64 eV. An alternate mechanism to form this first C-H bond was considered where H directly migrates from the O on benzoic acid to the C atom (R\*, depicted in Fig. 3a, to I<sub>3</sub>), forgoing both benzoic acid deprotonation and C-H bond formation *via* the anion-hydride mechanism (Fig. S3†). The activation barrier for this alternate mechanism is greater than 1 eV, suggesting that the hydride-mediated mechanism between the hydride and benzoate anion will be kinetically more favorable for C-H bond formation. Comparing relative rate constants for this competing path at a reaction temperature of 575 K (ref. 6) results in benzoic acid undergoing deprotonation nine orders of magnitude faster than C-H bond formation from the non-hydride route (eqn (S2)†). We also considered routes to C-H bond formation from which the H is passed to C from a surface O atom (not shown); however, these all proceed through either the hydride intermediate or by first placing the H onto the O atom of benzoate (*i.e.*, going back to molecularly adsorbed benzoic acid).

Once the C-H bond is formed through the hydride-mediated mechanism, structure I<sub>3</sub> can be considered as deprotonated phenylmethanediol. I<sub>3</sub> can further undergo hydrogenation to form benzaldehyde or decarboxylation to form benzene. In the case of hydrogenation, two H atoms are successively added on one of the O atoms of the deprotonated diol to form H<sub>2</sub>O that desorbs. This leads to

benzaldehyde adsorbed on O<sub>vac</sub> (I<sub>3</sub> + H<sub>2</sub> → P<sub>1</sub>\* + H<sub>2</sub>O), which proceeds thermodynamically uphill in energy by 0.99 eV. Finally, desorption of benzaldehyde from the O<sub>vac</sub> surface requires more than 2.8 eV. Alternatively, benzaldehyde can first desorb from I<sub>3</sub> (oxidized precursor of benzaldehyde) by leaving one O in O<sub>vac</sub> (refilling O<sub>vac</sub>) followed by the reformation of O<sub>vac</sub> (not shown).

Notably for the first C-H bond formation in benzoic acid, the required energy is at least 2.5 eV lower on the reduced surface than the fully oxidized surface (*i.e.*, compare 1.43 to 3.98 eV in Fig. 5 and 4, respectively). We conclude that carboxylic acid reduction on the TiO<sub>2</sub> surface will occur preferentially at O<sub>vac</sub> sites. Therefore, further mechanistic steps (*i.e.*, hydrogenation of benzaldehyde, *etc.*) were considered on the TiO<sub>2</sub> surface with O<sub>vac</sub>. The involvement of vacancy sites in the hydrodeoxygenation mechanism is supported by earlier experimental hypotheses that benzoic acid hydrogenation activity on reducible metal oxides increases with decreasing M-O bond strength (*i.e.*, higher O<sub>vac</sub> concentrations).<sup>6,28</sup>

Instead of hydrogenation to benzaldehyde, decarboxylation to benzene can occur from benzoate intermediates.<sup>81–83</sup> Decarboxylation reactions have been well-documented on metal oxides and confirmed experimentally using IR spectroscopy and CO<sub>2</sub> desorption.<sup>17</sup> Starting with I<sub>2</sub>, CO<sub>2</sub> can be eliminated from the adsorbed benzoate, resulting in a phenyl group co-adsorbed with a hydride in the O<sub>vac</sub> (I<sub>2</sub> → I<sub>10</sub> + CO<sub>2</sub>). Following the release of CO<sub>2</sub>, a 0.46 eV activation barrier is required to form the C-H bond and produce benzene adsorbed on the O<sub>vac</sub> (I<sub>10</sub> to P<sub>4</sub>\*). This C-H bond formation step to form benzene is thermodynamically favorable by 0.51 eV, with the desorption energy of benzene being 1.21 eV. Nonetheless, the energy barrier required to decarboxylate benzoate (at least 2.22 eV for I<sub>2</sub> to I<sub>10</sub>) is higher than that required to hydrogenate benzoate (1.43 eV for I<sub>2</sub> to



**Fig. 5** Reaction energy diagram (a) with optimized intermediate structures (b) of benzoic acid hydrogenation to benzaldehyde and decarboxylation to benzene on reduced anatase TiO<sub>2</sub> (001) with an O<sub>vac</sub>. Stable intermediate I<sub>1</sub> corresponds to Fig. 3f. All energies are referenced to gas phase benzoic acid and the reduced TiO<sub>2</sub> (001) surface. Structures with gas phase molecules are circled in blue, and adsorbed species in black, and transition states in red. Only the uppermost atomic layer is shown for the sake of clarity. Ti (gray), O (red), C (black), H (white), and O<sub>vac</sub> (dashed circle) are depicted.

I<sub>3</sub>) on the reduced anatase TiO<sub>2</sub> (001) surface. Hence, we also considered a decarboxylation pathway from I<sub>3</sub>.

This intermediate may undergo decarboxylation by shifting the hydrogen bound to the carbon of the carboxyl group to the carbon in the aromatic ring (I<sub>3</sub> → I<sub>11</sub>).<sup>69</sup> This hydrogen shift is an endothermic reaction with a barrier of 2.32 eV. Subsequently, the C–C bond between the carbon of the carboxyl group and the carbon in the aromatic ring can be broken, forming CO<sub>2</sub> and benzene adsorbed on the surface (I<sub>11</sub> → I<sub>12</sub>). The energy barrier for this C–C bond breaking is 0.26 eV. The desorption energies for CO<sub>2</sub> and benzene are 0.65 eV and 1.21 eV, respectively. Nonetheless, I<sub>3</sub> needs to surpass a much higher energy barrier (2.32 eV for I<sub>3</sub> to I<sub>11</sub>) on its way to decarboxylation than what is required for its further hydrogenation (0.99 eV for I<sub>3</sub> to P<sub>1</sub><sup>\*</sup>). Overall, these results indicate that it is energetically more favorable to hydrogenate benzoic acid to benzaldehyde on the reduced anatase TiO<sub>2</sub> (001) surface.

### 3.4. Benzaldehyde hydrogenation to benzyl alcohol and decarbonylation to benzene on reduced TiO<sub>2</sub> (001)

Next, the reaction path of benzaldehyde reduction to benzyl alcohol or benzene on the surface with an O<sub>vac</sub> was considered (Fig. 6). The decarbonylation of benzaldehyde to form benzene is examined through a mechanism similar to a 1,2-hydrogen shift,<sup>69,84,85</sup> where the H atom migrates to an adjacent C atom (P<sub>1</sub><sup>\*</sup> → I<sub>13</sub>). The migration of H in this step requires an energy barrier of 2.04 eV. Subsequent C–C bond breaking, resulting in adsorbed CO and benzene molecules (I<sub>13</sub> → I<sub>14</sub>), has a 0.42 eV energy barrier. Desorption of CO requires 0.86 eV, leaving benzene adsorbed on the O<sub>vac</sub> (P<sub>4</sub><sup>\*</sup>). As a final step, benzene desorbs from the reduced surface, as already described in the decarboxylation pathways of the previous section.

Alternatively, benzaldehyde hydrogenation to benzyl alcohol requires additional O–H formation and C–H bond



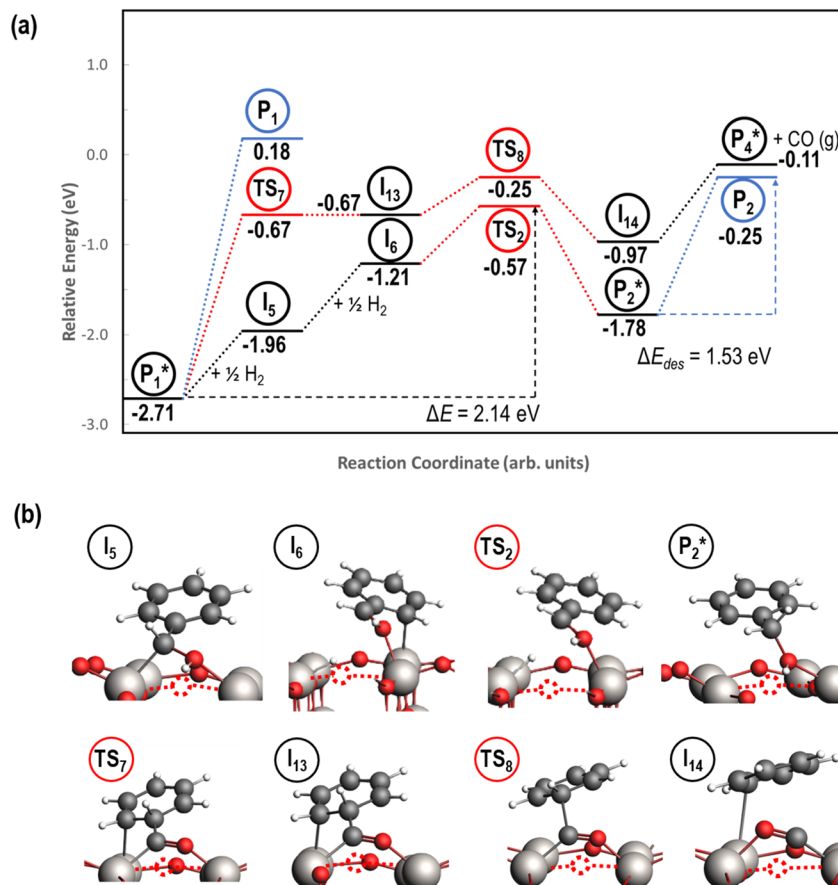


Fig. 6 Reaction energy diagram (a) with optimized intermediate structures (b) of benzaldehyde hydrogenation to benzyl alcohol on reduced anatase  $TiO_2$  (001) with an  $O_{vac}$ . Structures with gas phase molecules are circled in blue, adsorbed species in black, and transition states in red. Only the uppermost atomic layer is shown for the sake of clarity. Ti (gray), O (red), C (black), H (white), and  $O_{vac}$  (dashed circle) are depicted.

formation. The addition of H to form the O–H bond proceeds uphill in reaction energy by 0.75 eV ( $P_1^* \rightarrow I_5$ ), which ultimately forms a monoanionic ligand adsorbed on the  $O_{vac}$  (*i.e.*, benzyl alcohol missing a hydrogen on C). The subsequent co-adsorption of a hydride on the  $O_{vac}$  with the negatively charged ligand proceeds uphill by an additional 0.75 eV ( $I_5 \rightarrow I_6$ ). However, the C–H bond formation from the co-adsorbed species, resulting in adsorbed benzyl alcohol ( $I_6 \rightarrow P_2^*$ ), is exothermic and has the same barrier (*i.e.*, 0.64 eV) as the one reported in the previous section for the first C–H bond formation ( $I_2 \rightarrow I_3$ ) *via* the hydride-mediated mechanism. Finally, benzyl alcohol has a desorption energy of 1.53 eV, which is 1.36 eV lower than the desorption energy of benzaldehyde. Nevertheless, an energy barrier of 2.14 eV (see Fig. 6) needs to be surpassed to hydrogenate adsorbed benzaldehyde ( $P_1^*$ ) and form adsorbed benzyl alcohol ( $P_2^*$ ), which is larger than the 1.43 eV hydrogenation energy barrier reported for benzaldehyde formation from benzoate (see Fig. 5). This is largely attributed to a higher co-adsorption energy of the monoanionic ligand ( $I_6$ ) with the hydride in  $O_{vac}$  ( $\Delta E_{CoAds} = 0.84$  eV).

An alternate mechanism was explored for benzyl alcohol formation, reversing the order of H atom addition. The C–H

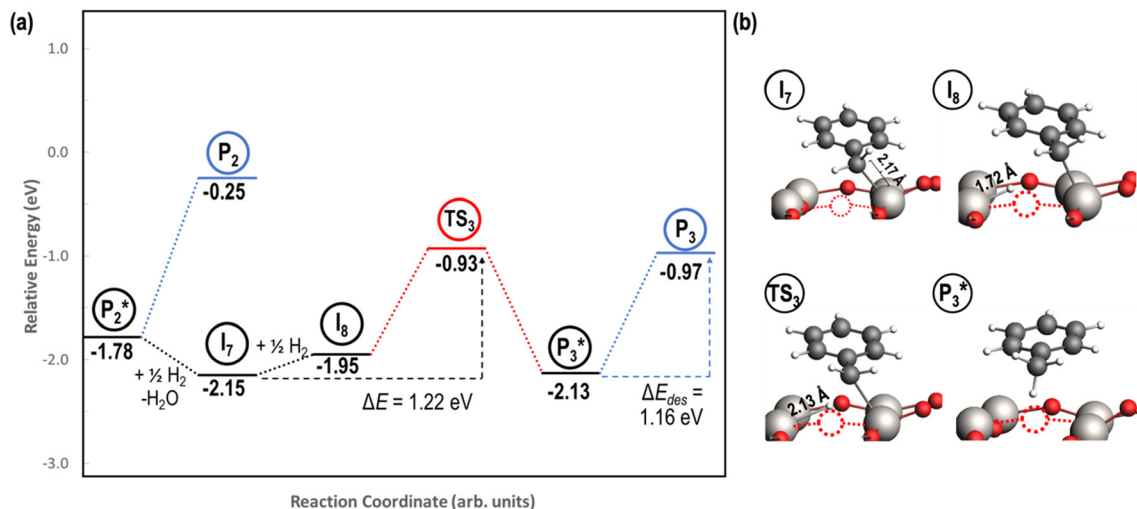
bond is formed first, followed by the O–H bond to form benzyl alcohol (Fig. S4†). A hydride-mediated mechanism for C–H formation is no longer possible in this path, as the ligand co-adsorbed in the  $O_{vac}$  is neutral in charge (*i.e.*, benzaldehyde). Co-adsorption of a hydride with benzaldehyde in  $O_{vac}$  is significantly unfavorable (not shown), with a co-adsorption energy of more than 2.60 eV. Instead, the alternative mechanism forms the first C–H bond from a proton adsorbed on the  $O_{3C}$  of  $TiO_2$  with a hydrogenation energy barrier (from  $S_1$  to  $TS_{S1}$ ) that is 0.21 eV lower than the one depicted in Fig. 6 (from  $P_1^*$  to  $TS_2$ ). This result highlights that alternative mechanisms may be competitive with the hydride-mediated mechanism if anionic ligand repulsion leads to a high co-adsorption energy.

### 3.5. Benzyl alcohol hydrogenation to toluene on reduced $TiO_2$ (001)

A mechanism of benzyl alcohol hydrogenation to toluene is proposed in Fig. 7. The most energetically viable mechanism of toluene production ( $P_3^*$ ) is directly from hydrogenating benzyl alcohol ( $P_2^*$ ). The removal of the hydroxyl group from







**Fig. 7** Reaction energy diagram (a) with optimized intermediate structures (b) of benzyl alcohol hydrogenation to toluene ( $P_3^*$ ) on reduced anatase  $TiO_2$  (001) with an  $O_{vac}$ . Structures with gas phase molecules are circled in blue, adsorbed species in black, and transition states in red. Only the uppermost atomic layer is shown for the sake of clarity. Ti (gray), O (red), C (black), H (white), and  $O_{vac}$  (dashed circle) are depicted.

benzyl alcohol *via* the desorption of  $H_2O$  ( $P_2^* \rightarrow I_7$ ) is thermodynamically favorable by 0.37 eV, leaving a benzyl ligand ( $I_7$ ) adsorbed in the vacancy (*i.e.*, a monoanionic ligand). The addition of a hydride co-adsorbed into the vacancy ( $I_7 \rightarrow I_8$ ) proceeds slightly uphill in reaction energy, attributed to a low co-adsorption energy of  $\Delta E_{CoAds} = 0.28$  eV between the two ligands (*i.e.*, only slightly net repulsive). Once again, the C–H bond formation to form toluene proceeds through a thermodynamically favorable reaction mechanism between a hydride and an electrophilic carbon center in a monoanionic ligand on an  $O_{vac}$ , with the reaction proceeding downhill by 0.18 eV ( $I_8 \rightarrow P_3^*$ ). The energy barrier required to hydrogenate benzyl alcohol to toluene, 1.22 eV (Fig. 7), is the lowest compared to those of benzaldehyde and benzyl alcohol formation (Fig. 5 and 6, respectively). Finally, toluene has the lowest desorption energy compared to previous hydrogenation intermediates, suggesting that toluene may be a prominent gas phase product. Notably, the direct formation of toluene from benzaldehyde by bypassing the formation of benzyl alcohol is very unfavorable, since an energy barrier of 4.89 eV (see Fig. S5†) needs to be surpassed to hydrogenate adsorbed benzaldehyde ( $P_1^*$ ) and form adsorbed benzyl ( $I_7$ ).

Thus, C–H bonds consistently form through co-adsorbed hydrides and ligands that have  $-1$  formal charges (*i.e.*, monoanionic ligands) bound in  $O_{vac}$ , with reasonably low kinetic barriers around or below 2 eV. The reaction energies of C–H bond formation between a hydride and the monoanionic species of interest (*e.g.*, benzoate, phenyl, benzyl) in an  $O_{vac}$  on  $TiO_2$  are also consistently thermodynamically favorable. However, high reaction temperatures may still be necessary to form  $O_{vac}$  and to overcome barriers associated with the co-adsorption of two anionic species in  $O_{vac}$  (*i.e.*,  $\Delta E_{CoAds}$ ). Partial pressures of hydrogen and, by extension, surface H coverages under reduction conditions will also affect the rates of C–H bond formation.

### 3.6. Microkinetic model of benzoic acid hydrogenation in an $O_{vac}$ site

A microkinetic model (MKM) that included reactions of  $H_2$  dissociation, benzoic acid adsorption, sequential hydrogenation, decarboxylation or decarbonylation, and desorption of products, consisting of 24 elementary steps (Table 1), was constructed to predict the relative rates of product formation under reaction conditions using the DFT reaction energies and barriers (as summarized in Fig. S6a† and corrected by the values reported in Table S1†). The availability of H adsorbed on O sites ( $H^{**}$ ) is derived from  $H_2$  heterolytic dissociative adsorption on the fully oxidized  $TiO_2$  (001) surface (Fig. S7†), with a reaction energy of  $-0.33$  eV and an energy barrier of 0.23 eV.

The detailed rate equations are described in eqn (S3).† The coupled system of 19 differential equations relating the rates of all intermediate surface species was solved simultaneously in the MKM. Gas phase concentrations were held constant, *i.e.*,  $P_{H_2} = P_{BZA} = 1$  bar. Note that the presence of surface hydroxyls was not considered on the reduced surface with  $O_{vac}$  under the dry conditions in which we performed MKM, since the formation of these species is not favorable under these conditions according to the thermodynamic analysis shown in Fig. S8.† For reaction temperatures varying from 450 to 900 K, the formation rate of each product was calculated using the steady state concentrations of the surface intermediates (*i.e.*, Fig. S9b†). The steady state rates of benzaldehyde, benzyl alcohol, toluene, and benzene formation are shown as a function of reaction temperature in Fig. 8a. While the rates of product formation are negligible at low temperatures, an increase in  $T$  to 650 K brings the rates within an order of a magnitude difference from hydrogenation turnover frequencies on single atom catalysts.<sup>86</sup> For example, the experimental turnover frequency of guaiacol



**Table 1** Elementary steps and reaction mechanism for hydrodeoxygenation, decarboxylation, and decarbonylation of benzoic acid on reduced anatase TiO<sub>2</sub> (001) surface. Equilibrated steps with partial equilibrium index between 0.45 and 0.55 at 540 K are indicated with circled arrow, and reaction steps with a degree of rate control higher than 0.1 at 540 K are indicated in bold

| Product                                                                                                                                                    |                                                                                                  | Benz |    |    | BAlD | BnOH | Tol |
|------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|------|----|----|------|------|-----|
| Path                                                                                                                                                       |                                                                                                  | D1   | D2 | D3 | H1   | H2   | H3  |
| 0                                                                                                                                                          | $\text{H}_2(\text{g}) + 2^{**} \rightleftharpoons 2\text{H}^{**}$                                | 0    | 0  | 1  | 1    | 1    | 1   |
| 1                                                                                                                                                          | $\text{R}(\text{g}) + * \rightleftharpoons \text{I}_1$                                           | 1    | 1  | 1  | 1    | 1    | 1   |
| 2                                                                                                                                                          | $\text{I}_1 \rightleftharpoons \text{I}_2$                                                       | 1    | 1  | 1  | 1    | 1    | 1   |
| 3                                                                                                                                                          | $\text{I}_2 \rightleftharpoons \text{I}_3$                                                       | 0    | 1  | 1  | 1    | 1    | 1   |
| 4                                                                                                                                                          | $\text{I}_3 + \text{H}^{**} \rightleftharpoons \text{I}_4 + **$                                  | 0    | 0  | 1  | 1    | 1    | 1   |
| 5                                                                                                                                                          | $\text{I}_4 + \text{H}^{**} \rightleftharpoons \text{P}_1^* + \text{H}_2\text{O}(\text{g}) + **$ | 0    | 0  | 1  | 1    | 1    | 1   |
| 6                                                                                                                                                          | $\text{P}_1^* \rightleftharpoons \text{P}_1(\text{g}) + *$                                       | 0    | 0  | 0  | 1    | 0    | 0   |
| 7                                                                                                                                                          | $\text{P}_1^* + \text{H}^{**} \rightleftharpoons \text{I}_5 + **$                                | 0    | 0  | 0  | 0    | 1    | 1   |
| 8                                                                                                                                                          | $\text{I}_5 + \text{H}^{**} \rightleftharpoons \text{I}_6 + **$                                  | 0    | 0  | 0  | 0    | 1    | 1   |
| 9                                                                                                                                                          | $\text{I}_6 \rightleftharpoons \text{P}_2^*$                                                     | 0    | 0  | 0  | 0    | 1    | 1   |
| 10                                                                                                                                                         | $\text{P}_2^* \rightleftharpoons \text{P}_2(\text{g}) + *$                                       | 0    | 0  | 0  | 0    | 1    | 0   |
| 11                                                                                                                                                         | $\text{P}_2^* + \text{H}^{**} \rightleftharpoons \text{I}_7 + \text{H}_2\text{O}(\text{g}) + **$ | 0    | 0  | 0  | 0    | 0    | 1   |
| 12                                                                                                                                                         | $\text{I}_7 + \text{H}^{**} \rightleftharpoons \text{I}_8 + **$                                  | 0    | 0  | 0  | 0    | 0    | 1   |
| 13                                                                                                                                                         | $\text{I}_8 \rightleftharpoons \text{P}_3^*$                                                     | 0    | 0  | 0  | 0    | 0    | 1   |
| 14                                                                                                                                                         | $\text{P}_3^* \rightleftharpoons \text{P}_3(\text{g}) + *$                                       | 0    | 0  | 0  | 0    | 0    | 1   |
| 15                                                                                                                                                         | $\text{I}_2 \rightleftharpoons \text{I}_{10} + \text{CO}_2(\text{g})$                            | 1    | 0  | 0  | 0    | 0    | 0   |
| 16                                                                                                                                                         | $\text{I}_{10} \rightleftharpoons \text{P}_4^*$                                                  | 1    | 0  | 0  | 0    | 0    | 0   |
| 17                                                                                                                                                         | $\text{I}_3 \rightleftharpoons \text{I}_{11}$                                                    | 0    | 1  | 0  | 0    | 0    | 0   |
| 18                                                                                                                                                         | $\text{I}_{11} \rightleftharpoons \text{I}_{12}$                                                 | 0    | 1  | 0  | 0    | 0    | 0   |
| 19                                                                                                                                                         | $\text{I}_{12} \rightleftharpoons \text{P}_4^* + \text{CO}_2(\text{g})$                          | 0    | 1  | 0  | 0    | 0    | 0   |
| 20                                                                                                                                                         | $\text{P}_1^* \rightleftharpoons \text{I}_{13}$                                                  | 0    | 0  | 1  | 0    | 0    | 0   |
| 21                                                                                                                                                         | $\text{I}_{13} \rightleftharpoons \text{I}_{14}$                                                 | 0    | 0  | 1  | 0    | 0    | 0   |
| 22                                                                                                                                                         | $\text{I}_{14} \rightleftharpoons \text{P}_4^* + \text{CO}(\text{g})$                            | 0    | 0  | 1  | 0    | 0    | 0   |
| 23                                                                                                                                                         | $\text{P}_4^* \rightleftharpoons \text{P}_4(\text{g}) + *$                                       | 1    | 1  | 1  | 0    | 0    | 0   |
| Path D1/D2 (decarboxylation to Benz): $\text{R}(\text{g}) = \text{P}_4(\text{g}) + \text{CO}_2(\text{g})$                                                  |                                                                                                  |      |    |    |      |      |     |
| Path D3 (decarbonylation to Benz): $\text{R}(\text{g}) + \text{H}_2(\text{g}) = \text{P}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ |                                                                                                  |      |    |    |      |      |     |
| Path H1 (hydrogenation to BAlD): $\text{R}(\text{g}) + \text{H}_2(\text{g}) = \text{P}_1(\text{g}) + \text{H}_2\text{O}(\text{g})$                         |                                                                                                  |      |    |    |      |      |     |
| Path H2 (hydrogenation to BnOH): $\text{R}(\text{g}) + 2 \text{H}_2(\text{g}) = \text{P}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$                       |                                                                                                  |      |    |    |      |      |     |
| Path H3 (hydrogenation to Tol): $\text{R}(\text{g}) + 3 \text{H}_2(\text{g}) = \text{P}_3(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$                      |                                                                                                  |      |    |    |      |      |     |

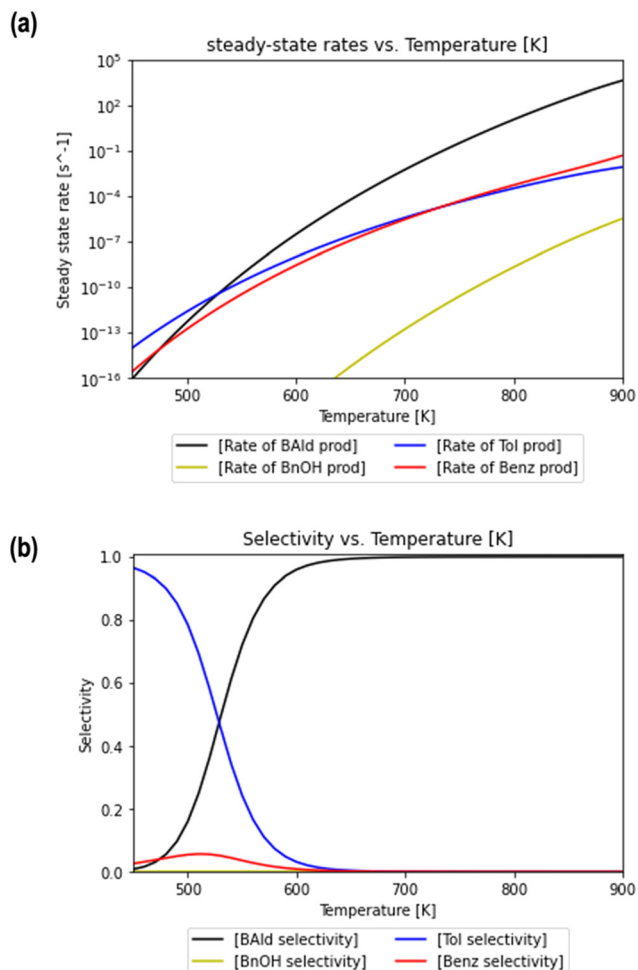
hydrodeoxygenation on Ag<sub>1</sub>/TiO<sub>2</sub> was determined to be near  $10^{-3} \text{ s}^{-1}$  at 573 K.<sup>32</sup>

Steady state rates of production were also used to calculate the relative selectivity of each product for the same temperature range (Fig. 8b). Two distinct temperature ranges are observed in the MKM, each of which has a specific product rate dominate. At low temperatures, the selectivity to toluene dominates over the selectivity to benzene and benzaldehyde. The small amount of benzene is formed through decarbonylation and not decarboxylation at these low *T* conditions as shown by a detailed rate analysis (Fig. S9a†). At higher temperatures, the selectivity to benzaldehyde consistently increases and is the highest amongst all products at temperatures of 540 K and above. Meanwhile, selectivity to benzene and toluene drops to zero as the temperature increases above 540 K. Over the complete temperature range, no selectivity to benzyl alcohol is observed.

Thus, the MKM predicts that the relative selectivity for toluene is the highest compared to those for all four products

at low temperatures till 540 K, while the relative selectivity of benzaldehyde dominates at temperatures of 540 K and higher. With the  $\text{O}_{\text{vac}}^*$  completely covered with adsorbed benzaldehyde ( $\text{P}_1^*$ ) for the most part of the investigated temperature range (see Fig. S9b†), this switch in selectivity from toluene to benzaldehyde as the temperature increases is a direct consequence of benzaldehyde desorption being more activated than its further hydrogenation (see Fig. 6). In agreement with the current MKM study, the limited experimental data available for benzoic acid HDO on metal oxides (*i.e.*, ZrO<sub>2</sub>, HfO<sub>2</sub>, TiO<sub>2</sub>) also report the production of toluene, benzene, and benzaldehyde at low temperatures and a steep increase in benzaldehyde selectivity as temperature increases.<sup>6</sup> Potential modifications in the entropy treatment and using an alternative pathway for benzaldehyde hydrogenation (as depicted in Fig. S4†) may affect the selectivity of benzene and toluene at low temperatures where the production rates are lower than  $10^{-10} \text{ s}^{-1}$  and the onset temperature where benzaldehyde becomes dominant (Fig. S10†). Nevertheless, the overall trend of





**Fig. 8** Rates of formation and selectivity of products predicted through the microkinetic model. Steady state rates (a) of benzaldehyde (black), benzyl alcohol (blue circles), toluene (dashed red), and benzene (dotted green) production are plotted as a function of reaction temperature. The relative selectivity of each product (b) is calculated using rates of formation at steady state at various temperatures. The coverages of select surface intermediates at different temperatures are included in Fig. S9b†

increase in benzaldehyde selectivity with increasing temperature remains consistent.

We further analyze the MKM using the degree of rate control at the crucial temperature of 540 K (Table 1, Fig. S11a†), where several products are observed. Almost all elementary steps contribute insignificantly to the overall reaction rate when perturbed, with a degree of rate control near zero. The reaction steps with the degree of rate control higher than 0.1 involve benzaldehyde desorption, decarbonylation *via* C–C bond cleavage and further hydrogenation to benzyl alcohol *via* hydride-mediated C–H bond formation. The results suggest that these elementary steps have significant impacts on the overall benzoic acid consumption. Additionally, the degree of selectivity control<sup>71</sup> quantifies how significantly each elementary step contributes to the relative increase in selectivity with respect to each product (Fig. S11b†).

The partial equilibrium index (PEI) is also calculated for each elementary step at 540 K (Table 1, Fig. S11c†). A majority of the elementary steps are not near equilibrium, which makes it difficult with PEI alone to pinpoint any one reaction that is the rate-determining step of the system. Eight elementary steps can be considered near-equilibrated with a PEI between 0.45 and 0.55. Contrarily, no steps have PEIs near zero, which would generally correspond to reactions with very low forward reaction rates. The PEI also confirms the results from the degree of rate control, namely that the reactions with a high degree of rate control are also far from equilibrium (*i.e.*, benzaldehyde desorption, decarbonylation, and further hydrogenation). In summary, the PEIs and degrees of rate control give a comprehensive overview of the microkinetic model and suggest which elementary steps should be targeted through rational catalyst design. For example, modifications to the catalyst that can alter the desorption, decarbonylation, or further hydrogenation of benzaldehyde (*i.e.*, the non-equilibrated elementary steps with the highest degree of rate control) are expected to have significant impacts on the overall reaction according to the microkinetic model. Though not represented mathematically in the MKM that predicts rate per vacancy site, promoting vacancy formation would also generate more active sites and enhance the rate.

## 4. Conclusions

C–H bond formation to four aromatic products (*i.e.*, benzaldehyde, benzyl alcohol, toluene, and benzene) on anatase  $\text{TiO}_2$  (001) can occur through a hydride-mediated mechanism on surface  $\text{O}_{\text{vac}}$  sites. In this mechanism, a negatively charged monoanionic intermediate ligand reacts with a favorable reaction energy with a hydride coadsorbed in  $\text{O}_{\text{vac}}$ . The overall reaction energy diagram of benzoic acid hydrodeoxygenation was constructed using plausible intermediates and kinetic barriers related to C–H bond formation as well as decarboxylation and decarbonylation. Finally, a microkinetic model was constructed using the overall mechanism and DFT energetics. The MKM suggests that selectivity to toluene is favored over the other three products at low temperatures, while benzaldehyde selectivity dominates at moderate-to-high temperatures. Competing mechanisms such as those for benzaldehyde hydrogenation, decarbonylation, and desorption result in the model predicting different product formation rates and selectivities. MKM analysis through degree of rate control and partial equilibrium index calculations shows several elementary steps that are far from equilibrium and thus can be targeted in the future for potentially significant impacts on the overall rate and selectivity of benzoic acid hydrodeoxygenation.

## Data availability

Data are available within the article and its ESI.†



## Disclaimer

The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Manufacturing Office Award Number DE-EE0007897 awarded to the REMADE Institute, a division of Sustainable Manufacturing Innovation Alliance Corp. Computational resources were provided through the Extreme Science and Engineering Discovery Environment (XSEDE), supported by the National Science Foundation (grant no. ACI-1548562).

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