

# Rationalizing Catalytic Performances of Mo/W-(Oxy)Carbides for Hydrodeoxygenation Reaction

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Hydrodeoxygenation (HDO) reactions are among the most important reactions for the valorization of biomass to value-added chemicals. Transition metal carbides (TMCs) are promising alternative HDO catalysts to platinum group metals. However, it is known that these TMCs have the tendency to partially oxidize themselves in the presence of oxygen or oxygen-containing compounds, which makes it a challenge to identify the nature of the true active site under relevant reaction conditions. In this paper, first, we analyze the surface structure of transition metal oxycarbides (TMOs), that is,  $\text{Mo}_2\text{CO}_x$  and  $\text{W}_2\text{CO}_x$ . Further, taking the HDO of *n*-butyric acid to *n*-butane with hydrogen as

an example, we rationalize the differences in HDO performances of TMOs as compared to TMCs ( $\text{Mo}_2\text{C}$  and  $\text{W}_2\text{C}$ ) using density functional theory, ab initio molecular dynamics, and microkinetic modelling. It is found that the  $\text{O}^*$  domains on the surface of TMOs enhance the HDO activity by easing the dissociation of the C-O bond and promoting the hydrogenation reactions, as compared to pure TMCs. Furthermore, microkinetic modelling analysis shows that  $\text{Mo}_2\text{CO}_x$  is a more active and selective catalyst for alkane production compared to  $\text{Mo}_2\text{C}$ ,  $\text{W}_2\text{C}$ , and  $\text{W}_2\text{CO}_x$ . These insights could guide the manipulation of efficient carbide-based HDO catalysts for biomass conversion.

## 1. Introduction

To mitigate the negative impact of the use of fossil resources on our climate renewable feedstocks, sustainable conversions are needed to make chemicals, materials and fuels. Biomass is such a renewable feedstock. However, the oxygen content in biomass is typically too high for current applications; therefore, deoxygenations are needed. As a case in point the catalytic deoxygenation of lipids present in biomass is required to obtain chemicals such as alkenes, alkanes, and alcohols.<sup>[1,2]</sup> Thus, hydrodeoxygenation (HDO) of long-chain fatty acids (LCFAs) has attracted much attention for the conversion of biomass to value-added chemicals.<sup>[3,4]</sup> Platinum group metals (PGMs) such as platinum (Pt) and palladium (Pd) have been shown to be viable catalysts for HDO.<sup>[5]</sup> While these catalysts show good reaction activity, limited availability and associated high costs make them unattractive for industrial use. Therefore, efforts are needed to find highly effi-

cient, cheap and sustainable alternatives to PGMs for HDO reactions.

Transition metal carbides (TMCs) have been shown to be viable alternatives to PGMs for HDO reactions.<sup>[6]</sup> Especially, tungsten carbide ( $\text{W}_2\text{C}$ ) and molybdenum carbide ( $\text{Mo}_2\text{C}$ ) have received much attention<sup>[7–11]</sup> since Levy and Boudart<sup>[12]</sup> demonstrated that these materials exhibit catalytic properties like noble metal-based catalysts. These authors attribute the PGM-like properties of TMCs to the carbon incorporation in the metal lattice, leading to a higher d-band electronic density of states, closer to the Fermi level. Decades later, Iglesia et al.<sup>[13]</sup> showed that WC and  $\text{W}_2\text{C}$  catalyzed hydrogenolysis, hydrogenation, and dehydrogenation reactions with high selectivity, which were previously only documented for Pt, Ir, and Au metals. Choi et al. further demonstrated that increased carburization (carbon content) of the transition metal increased its PGM-like catalytic properties.<sup>[14]</sup> More recently, many research groups have studied structure-activity relationships of TMCs for hydrogenation, dehydrogenation, HDO, and many other reactions, and successfully demonstrated TMCs' ability to catalyze a wide range of reactions.<sup>[8,10,11,15,16]</sup> Prats et al. have summarized most of these findings and other recent progress in utilizing TMCs as supports for catalytic metal particles.<sup>[17]</sup> The interesting behavior and versatility of reactions TMCs could catalyze has incentivized research into their intrinsic structure-activity relationships.

However, a potential downside of using these TMCs as catalysts is the ease at which they (partially) oxidize in the presence of oxygen or oxygen-containing compounds, thereby resulting in the formation of transition metal oxycarbides (TMOs), that is,  $\text{Mo}_2\text{CO}_x$  and  $\text{W}_2\text{CO}_x$ . Although not much research on the nature of  $\text{W}_2\text{CO}_x$  is available at this moment, the activity and nature of molybdenum oxycarbide ( $\text{Mo}_2\text{CO}_x$ ) have been explored.<sup>[18]</sup> Chen et al. studied the effects of oxygen content on rates and

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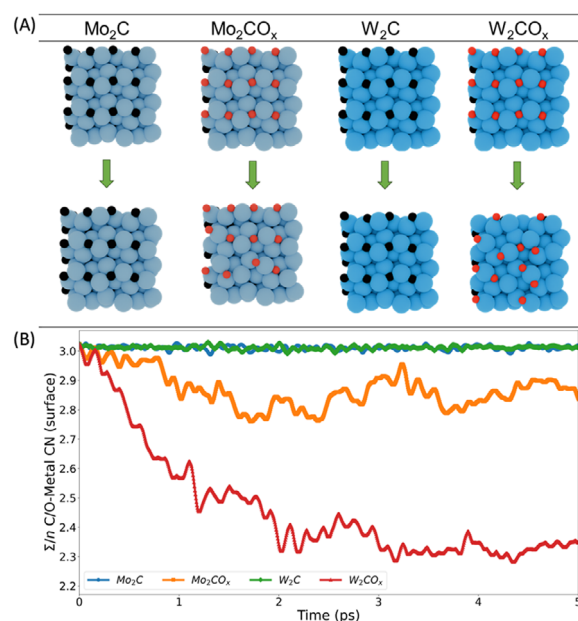
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selectivity of *m*-Cresol HDO for toluene synthesis.<sup>[19]</sup> These authors showed that exposure to molecular oxygen resulted in oxygen (0.23 O/Mo<sub>bulk</sub>) being deposited on Mo<sub>2</sub>C at low oxidant pressure (1 kPa) and temperature (333 K), and that the toluene synthesis rate was reduced 10-fold due to poisoning of the active surface metal-like sites by adsorbed oxygen. Also, Kumar et al. reported that oxygen deposition (0.3 O/Mo<sub>bulk</sub>) from the reactant oxygenate was observed during the HDO of acetic acid.<sup>[20]</sup> Density functional theory (DFT) and microkinetic reactor modelling study by Ammal et al. showed that oxyphilic Mo<sub>2</sub>C (100) surface is active for HDO of glycerol to hydroxypropanal.<sup>[21]</sup> These authors, in their model, assume that Mo<sub>2</sub>C surface is fully oxygenated with acid-base (OH, O) pairs, that is, 0.5 monolayer of oxygen (ML<sub>O</sub>). The -OH groups promote H<sub>2</sub>O formation, resulting in oxygen vacancies and exposed active Mo sites which promote the C-O cleavage. Kurlov et al. demonstrated that the dry reforming of methane was promoted over oxygen-modified 2D-Mo<sub>2</sub>C, compared to Mo<sub>2</sub>C, where they assume that the surface of Mo<sub>2</sub>C is occupied with oxygen (0.67 ML<sub>O</sub>).<sup>[22]</sup>

Based on the aforementioned studies, it is expected that catalytic HDO of free fatty acids on TMCs (Mo<sub>2</sub>C, W<sub>2</sub>C) would result in high levels of oxygen being deposited on the catalyst surface, essentially forming TMOCs (Mo<sub>2</sub>CO<sub>x</sub>, W<sub>2</sub>CO<sub>x</sub>). Therefore, to model such a surface, we take inspiration from experiments by Ovári et al.<sup>[23]</sup> where they demonstrated the complete removal of surface carbon (as CO) from Mo<sub>2</sub>C (100) upon interaction with O<sub>2</sub> at 500–600 K using mass spectrometry. The C-vacancies are then filled with oxygen atoms. Later, Shi et al.<sup>[24]</sup> also provided mechanisms for this surface carbon removal as CO and chemisorption of oxygen over Mo<sub>2</sub>C (011, 101) surfaces. More recently, Sun et al. show that deposition of a layer of oxygen on the Mo<sub>2</sub>C surface to form Mo<sub>2</sub>CO<sub>x</sub> species increases the stability of the catalyst and promotes C-O bond scission (compared to Mo<sub>2</sub>C) for CO<sub>2</sub> hydrogenation reaction.<sup>[25]</sup> Hence, in our study, we utilize a similar model where the carbon atoms in the top layer of the widely studied Mo<sub>2</sub>C and W<sub>2</sub>C catalysts<sup>[26–28]</sup> are substituted with oxygen to represent the TMOCs surface, corresponding to 0.5 ML<sub>O</sub>, as depicted in Figure 1A. The stability of such surfaces (oxygen-modified Mo<sub>2</sub>C) is supported by the work of Likith et al.<sup>[29]</sup> and Li et al. as well.<sup>[30]</sup> These authors evaluated the thermodynamic stabilities of different compositions of molybdenum oxycarbides formed from Mo<sub>2</sub>C in the reduction condition of H<sub>2</sub> evolution reaction and the results were validated by experiments. They show that Mo<sub>2</sub>CO<sub>x</sub> is stable under reduction conditions with a C:O ratio of 2:1, which is consistent with the model employed in this study.

It is important to understand how the presence of oxygen on the surface alters the activity and selectivity of TMOCs compared to pure TMCs for HDO of biobased feedstock. In this work, we rationalized the catalytic HDO performances of TMCs (Mo<sub>2</sub>C, W<sub>2</sub>C), and TMOCs (Mo<sub>2</sub>CO<sub>x</sub>, W<sub>2</sub>CO<sub>x</sub>) by a comprehensive reaction mechanism study of the HDO reaction of *n*-butyric acid to *n*-butane. DFT reaction energies in combination with MKM were used in identifying the critical intermediates, rate-determining elementary reaction step(s), and the activity and selectivity differences of the catalysts studied. Based on these analyses, it is found that C–OH bond dissociation is one of the most critical



**Figure 1.** (A) Evolution of the catalytic surfaces at a reaction temperature of 623 K, simulated for 5 ps using AIMD. (B) The average coordination number (CN) of C/O-Metal (Mo/W) per surface C/O over time. NOTE: *n* is the number of C or O atoms on the surface, that is, 12.

steps and TMOCs are more active and selective toward alkanes compared to TMCs.

## 2. Results and Discussion

### 2.1. Carbide and Oxycarbide Model Rationalization

Butyric acid was chosen in this study as a model compound for fatty acids, as it possesses a carboxyl acid moiety and an aliphatic tail, which are also present in fatty acids. For the TMC surface models, we chose the stable Mo<sub>2</sub>C (101) and W<sub>2</sub>C (101) terminations, while for TMOCs we took inspiration from previous experimental<sup>[19,20,22,23]</sup> and theoretical studies,<sup>[24,29,30]</sup> and built models in which the top-layer C atoms in Mo<sub>2</sub>C (101) and W<sub>2</sub>C (101) were replaced by O atoms, as shown in Figure 1A.

From the initial static DFT geometry relaxations, no significant surface reconstruction was observed for both the carbide and oxycarbide surfaces. To further evaluate the surface structure, we performed AIMD simulations of the four catalysts under study to better understand the nature of active sites (metal center) under reaction conditions. We start the simulations using static DFT optimized geometries. Figure 1A shows the initial geometries (top) of the clean catalytic surfaces, and final geometries (bottom) after 5 ps of AIMD simulation at 623 K. Further, we quantified (Figure 1B) the change in coordination environment of the active surface metal site by calculating the average C-Metal (Mo or W) coordination number (CN) per surface C in TMCs, and O-Metal CN per surface O in TMOCs. The results reveal that TMC surfaces are stable with negligible surface reconstruction, while TMOc surfaces are much more dynamic, as the surface continuously undergoes reconstruction, that is, the average CN

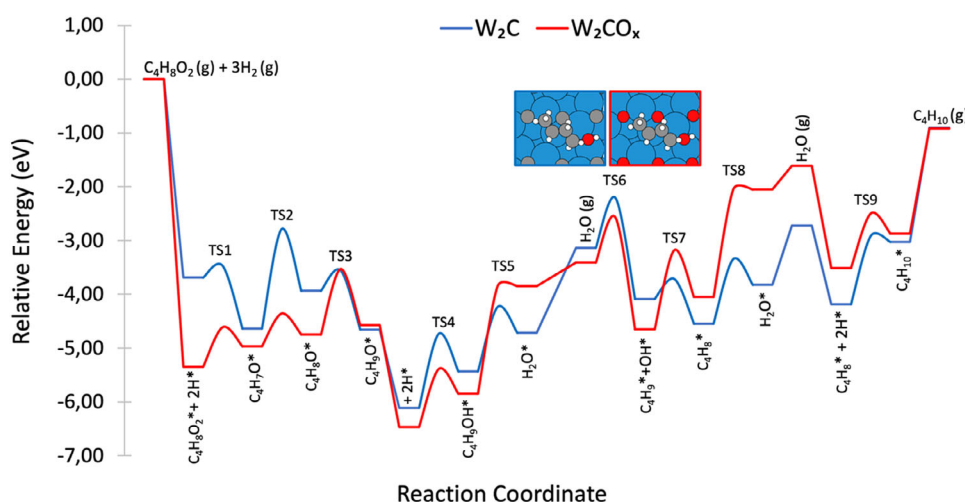
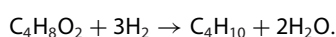


Figure 2. The reaction energy diagram for the HDO reaction of *n*-butyric acid over  $W_2C$  and  $W_2CO_x$  catalysts.

of O-Metal on the surface changes from 3.00 to  $\sim 2.85$  in the case of  $Mo_2CO_x$ , and changes from 3.00 to  $\sim 2.40$  in the case of  $W_2CO_x$ . We speculate that a reduction in these CNs leads to a more active metal center. While the CN changes, these surface O atoms stay on the surface and no diffusion into the sublayer was observed.

## 2.2. HDO Reaction Mechanism

We studied the HDO reaction mechanism of butyric acid over  $Mo_2C$  (101),  $W_2C$  (101),  $Mo_2CO_x$  (101), and  $W_2CO_x$  (101) catalysts. In all cases, we start with a clean slab, butyric acid and three molecules of molecular  $H_2$  to produce butanal, followed by butanol, butene, and butane products. This sequential manner is based on experimental observations. For example, Stellwagen et al.<sup>[10]</sup> and Marlene et al.<sup>[16]</sup> showed in their work the stearic acid concentration and product distribution over time of  $Mo_2C$  and  $W_2C$ . Their product distribution shows that  $Mo_2C$  and  $W_2C$  follow the HDO pathway of substrate reduction to aldehyde, followed by alcohol, alkene and alkane for the removal of oxygen content from stearic acid. Further, we have shown in our previous work,<sup>15</sup> H- species on the surface can easily hop over the surface under reaction conditions ( $T = 623$  K,  $p_{H_2} = 30$  bar). Subsequently, the reactant is adsorbed on the surface, and then the elementary steps take place on the surface (denoted by \*). Eventually, the final product, that is, butane and two molecules of water ( $H_2O$ ) are desorbed from the surface. Throughout the text, the carbon atom of the acidic group is referred to as C1. The overall reaction is as following.



## 2.3. HDO over $W_2C$ and $W_2CO_x$

The reaction energy profiles for the HDO reaction over  $W_2C$  and  $W_2CO_x$  surfaces are shown in Figure 2. First, the butyric acid and

dissociative  $H_2$  adsorption (in a homolytic manner) over W-W metal active sites is an exothermic process over  $W_2C$  ( $\Delta E = -3.69$  eV) and  $W_2CO_x$  ( $\Delta E = -5.35$  eV). Butyric acid ( $C_4H_8O_2^*$ ) then undergoes C—OH activation via TS1 and forms  $C_4H_7O^*$  and  $OH^*$  exothermically over  $W_2C$  ( $E_a = 0.22$  eV,  $\Delta E = -0.99$  eV), and endothermically over  $W_2CO_x$  ( $E_a = 0.74$  eV,  $\Delta E = 0.38$  eV). Here, we also consider a pathway where hydrogenation of the carbonyl group happens first instead of C—OH activation over all four catalysts under study. It was found that the resulting intermediate ( $C_3H_7C(OH)_2^*$ ) from hydrogenation reaction is at least 0.80 eV less stable than the intermediate ( $C_4H_7O^* + OH^*$ ) upon C—OH cleavage. The difference in the C—OH activation barrier in TS1 is due to the strong adsorption of butyric acid over  $W_2CO_x$ . The butyric acid is adsorbed over  $W_2CO_x$  via bidentate W—O bonds (oxygen from butyric acid), compared to monodentate W—O bond in  $W_2C$ . The terminal C atom (C1) in  $C_4H_7O^*$  is then hydrogenated via TS2 to produce butanal ( $C_4H_8O^*$ ) in the case of  $W_2C$  ( $E_a = 1.84$  eV,  $\Delta E = 0.70$  eV); this step is kinetically challenging as C1 is strongly adsorbed on W atom and resists hydrogenation. This hydrogenation step is much easier in the case of  $W_2CO_x$  ( $E_a = 0.61$  eV,  $\Delta E = 0.22$  eV) due to the weak physisorption of C1 on W-atom. Subsequently, the C1 atom in  $C_4H_8O^*$  is hydrogenated again via TS3 to produce  $C_4H_9O^*$ , a precursor for butanol ( $C_4H_9OH^*$ ) formation. The O atom in  $C_4H_9O^*$  is then hydrogenated via TS4 to produce  $C_4H_9OH^*$  over  $W_2C$  ( $E_a = 1.38$  eV,  $\Delta E = 0.69$  eV), which is similar to  $W_2CO_x$  ( $E_a = 1.08$  eV,  $\Delta E = 0.62$  eV).  $C_4H_9OH^*$  then undergoes C—OH activation via TS6 (local structures in Figure 2) to produce  $C_4H_9^*$  and  $OH^*$  over  $W_2C$  ( $E_a = 0.93$  eV,  $\Delta E = -0.94$  eV), which is also similar but slightly easier in  $W_2CO_x$  ( $E_a = 0.84$  eV,  $\Delta E = -1.24$  eV), implying a better activity of  $W_2CO_x$  for deoxygenation. The C1 atom in  $C_4H_9^*$  then undergoes deprotonation via TS7 to produce butene ( $C_4H_8^*$ ). This process is much easier over  $W_2C$  ( $E_a = 0.37$  eV,  $\Delta E = -0.46$  eV) than over  $W_2CO_x$  ( $E_a = 1.47$  eV,  $\Delta E = -0.60$  eV). However, instead of undergoing deprotonation to  $C_4H_8^*$ ,  $C_4H_9^*$  can readily hydrogenate to form  $C_4H_{10}^*$  via TS9. This is much easier over  $W_2CO_x$  ( $E_a = 1.01$  eV,  $\Delta E = 0.64$  eV) compared to dehydrogenation to  $C_4H_8^*$ . The barriers TS7 and

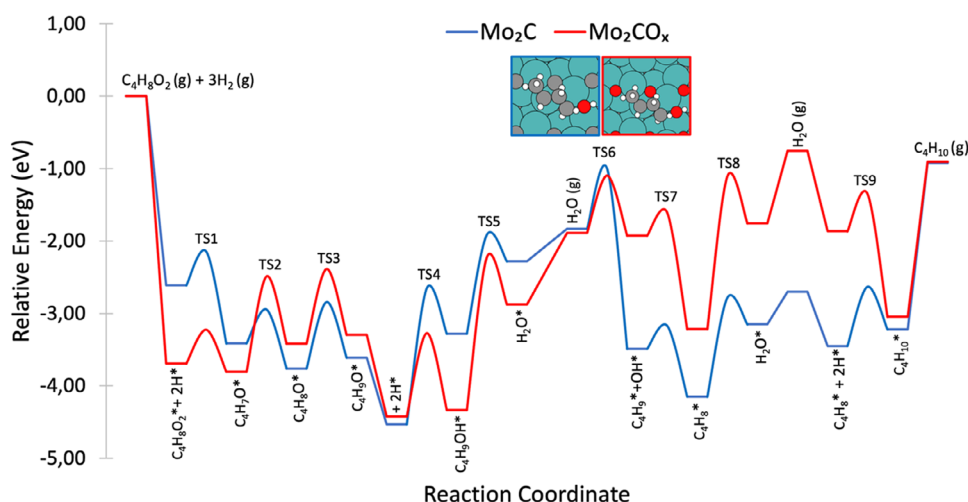


Figure 3. The reaction energy diagram for the HDO reaction of *n*-butyric acid over  $\text{Mo}_2\text{C}$  and  $\text{Mo}_2\text{CO}_x$  catalysts.

TS9 imply that these two steps compete during the reaction. The final product,  $\text{C}_4\text{H}_{10}^*$ , can then be desorbed requiring a desorption energy of 2.12 eV over  $\text{W}_2\text{C}$  and 1.95 eV over  $\text{W}_2\text{CO}_x$ . Also, the  $\text{OH}^*$  species on the surface can be hydrogenated to produce water ( $\text{H}_2\text{O}^*$ ) via TS5/8. Water formation over  $\text{W}_2\text{CO}_x$  ( $E_a = 2.00$  eV,  $\Delta E = 2.00$  eV) is kinetically and thermodynamically much more difficult compared to  $\text{W}_2\text{C}$  ( $E_a = 1.20$  eV,  $\Delta E = 0.62$  eV), suggesting the presence of excess  $\text{H}^*$  species over  $\text{W}_2\text{CO}_x$  surface.

## 2.4. HDO over $\text{Mo}_2\text{C}$ and $\text{Mo}_2\text{CO}_x$

Figure 3 illustrates the HDO reaction energy diagram for  $\text{Mo}_2\text{C}$  and  $\text{Mo}_2\text{CO}_x$ . The reaction energies over  $\text{Mo}_2\text{C}$  studied in our previous work<sup>[15]</sup> were used to compare with the reactivity of  $\text{Mo}_2\text{CO}_x$  catalyst studied in this work. Again, butyric acid is adsorbed over  $\text{Mo}_2\text{CO}_x$  together with homolytic  $\text{H}_2$  dissociative adsorption over Mo-Mo metal active sites ( $\Delta E = -3.69$  eV). Butyric acid,  $\text{C}_4\text{H}_8\text{O}_2^*$ , undergoes C—OH activation via TS1 and forms  $\text{C}_4\text{H}_7\text{O}^*$  and  $\text{OH}^*$  in the case of  $\text{Mo}_2\text{CO}_x$  ( $E_a = 0.47$  eV,  $\Delta E = -0.11$  eV), while it is kinetically difficult and thermodynamically more favorable over  $\text{Mo}_2\text{C}$  ( $E_a = 0.45$  eV,  $\Delta E = -0.80$  eV). The C1 atom in  $\text{C}_4\text{H}_7\text{O}^*$  is then hydrogenated via TS2 to produce butanal,  $\text{C}_4\text{H}_8\text{O}^*$  ( $E_a = 1.32$  eV,  $\Delta E = 0.39$  eV). This process is kinetically less demanding in  $\text{Mo}_2\text{C}$  ( $E_a = 0.46$  eV,  $\Delta E = -0.35$  eV) because of weaker Mo-C1 interactions compared to  $\text{Mo}_2\text{CO}_x$ . Further, the C1 atom in  $\text{C}_4\text{H}_8\text{O}^*$  is hydrogenated via TS3 to produce  $\text{C}_4\text{H}_9\text{O}^*$  ( $E_a = 1.03$  eV,  $\Delta E = 0.12$  eV), which is kinetically and thermodynamically similar to that over  $\text{Mo}_2\text{C}$  ( $E_a = 0.92$  eV,  $\Delta E = 0.15$  eV). The O atom in  $\text{C}_4\text{H}_9\text{O}^*$  is then hydrogenated via TS4 to produce butanol,  $\text{C}_4\text{H}_9\text{OH}^*$  ( $E_a = 1.15$  eV,  $\Delta E = 0.09$  eV). This process is much more difficult over  $\text{Mo}_2\text{C}$  ( $E_a = 1.88$  eV,  $\Delta E = 1.25$  eV), as  $\text{O}^*$  is strongly stabilized over the Mo-Mo center.  $\text{C}_4\text{H}_9\text{OH}^*$  undergoes C—OH activation via TS6 (local structures in Figure 3) to produce  $\text{C}_4\text{H}_9^*$  and  $\text{OH}^*$  ( $E_a = 0.79$  eV,  $\Delta E = -0.04$  eV). This step is kinetically slightly difficult over  $\text{Mo}_2\text{C}$  ( $E_a = 0.83$  eV,  $\Delta E = -1.66$  eV); however, it

is thermodynamically very favorable compared to  $\text{Mo}_2\text{CO}_x$ . The C1 atom in  $\text{C}_4\text{H}_9^*$  then undergoes deprotonation via TS7 to produce butene,  $\text{C}_4\text{H}_8^*$  ( $E_a = 0.32$  eV,  $\Delta E = -1.29$  eV), which is more favorable thermodynamically compared to  $\text{Mo}_2\text{C}$  ( $E_a = 0.32$  eV,  $\Delta E = -0.66$  eV). Like the case of  $\text{W}_2\text{C}$  and  $\text{W}_2\text{CO}_x$ ,  $\text{C}_4\text{H}_9^*$  can instead be hydrogenated to form  $\text{C}_4\text{H}_{10}^*$  ( $E_a = 0.52$  eV,  $\Delta E = -1.18$  eV) via TS9. This step is much more favorable over  $\text{Mo}_2\text{CO}_x$  than over  $\text{Mo}_2\text{C}$  ( $E_a = 0.82$  eV,  $\Delta E = 0.23$  eV). In the case of  $\text{Mo}_2\text{CO}_x$ , the carbon chain could easily be hydrogenated to produce butane,  $\text{C}_4\text{H}_{10}^*$ , but for  $\text{Mo}_2\text{C}$ , the pathway to form  $\text{C}_4\text{H}_8^*$  is more favorable. The final product,  $\text{C}_4\text{H}_{10}^*$ , can then be desorbed with barriers of 2.14 eV for  $\text{Mo}_2\text{CO}_x$ , and 2.30 eV for  $\text{Mo}_2\text{C}$ , individually. Compared to  $\text{Mo}_2\text{CO}_x$  ( $E_a = 2.11$  eV,  $\Delta E = 1.46$  eV), water formation is kinetically and thermodynamically easier over  $\text{Mo}_2\text{C}$  ( $E_a = 1.37$  eV,  $\Delta E = 1.00$  eV).

## 2.5. Microkinetic Modelling (MKM)

From static DFT calculations, it is indicated that hydrogenation of unsaturated hydrocarbons is much easier over  $\text{W}_2\text{CO}_x$  and  $\text{Mo}_2\text{CO}_x$  surfaces compared to  $\text{W}_2\text{C}$  and  $\text{Mo}_2\text{C}$ . Therefore, these hydrogenation steps essentially guide their selectivity toward alkane/alkene products. However, merely looking at the kinetics and thermodynamics of different elementary reaction steps involved is not enough to compare the activity of these catalysts. Hence, we performed microkinetic modelling (MKM) using the static DFT results and experimental reaction temperature (623 K) and pressure ( $p_{\text{H}_2} = 30$  bar) to obtain the macroscopic properties such as surface coverages, Campbell's degree of rate control (DRC) coefficients,<sup>[31]</sup> apparent activation energies ( $E_{\text{app}}$ ), and selectivity toward alkane/alkene products.

## 2.6. Surface Coverages

The steady-state surface coverages are shown in Figure 4. In the case of  $\text{Mo}_2\text{C}$  (Figure 4A), we see the presence of  $\text{O}^*$  domains



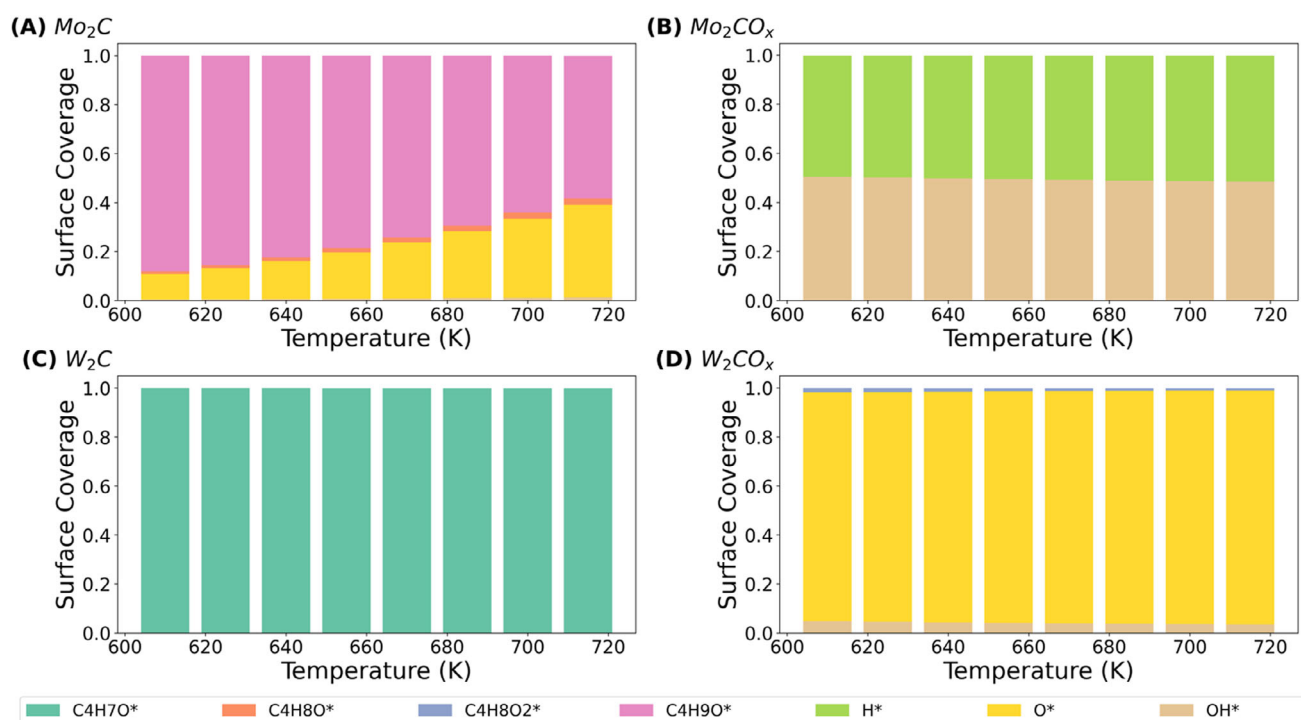


Figure 4. Steady state surface coverage as a function of temperature. Only the species with coverage > 0.005 are shown in the plots.

on the surface, hinting toward the possible formation of oxycarbide surface during the HDO reaction. However, that is not the case in  $\text{W}_2\text{C}$  (Figure 4C), where the reaction is very slow and the surface is dominated by the presence of  $\text{C}_4\text{H}_7\text{O}^*$ , a precursor for butanal ( $\text{C}_4\text{H}_8\text{O}$ ) formation. On the other hand, in the case of  $\text{Mo}_2\text{CO}_x$  (Figure 4B), the surface is mostly dominated by  $\text{OH}^*$  and  $\text{H}^*$ , as water ( $\text{H}_2\text{O}^*$ ) formation is kinetically and thermodynamically a difficult step ( $E_a = 2.11$  eV,  $\Delta E = 1.46$  eV). This shows that the  $\text{Mo}_2\text{CO}_x$  surface is robust and none of the intermediates and products are too stable on the surface, which makes the reaction faster. Also, the availability of excess  $\text{H}^*$  species promotes the reaction, making it a more active catalyst than the rest. Whereas the surface of  $\text{W}_2\text{CO}_x$  (Figure 4D) is dominated by  $\text{O}^*$  species, which shows that the surface is more robust than  $\text{W}_2\text{C}$ ; but since the water formation ( $\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^*$ ) is too difficult ( $E_a = 2.00$  eV,  $\Delta E = 2.00$  eV), the availability of excess  $\text{H}^*$  promote the reactions.

## 2.7. Apparent Activation Energy ( $E_{\text{app}}$ )

The apparent activation energies for the different catalysts are shown in Figure 5. It is evident that the activity of carbide catalysts increases as a function of temperature. While in the case of oxycarbide catalyst, the temperature does not influence the activity. Based on these results, we could conclude that  $\text{Mo}_2\text{CO}_x$  is the most active catalyst for butyric acid HDO at the reaction temperature of 623 K, with an apparent activation barrier of 2.40 eV, followed by  $\text{W}_2\text{CO}_x$  over which the apparent activation barrier is 2.70 eV. Both carbide catalysts are much less active compared to their oxycarbide counterparts. It is important to note that the higher HDO activity of  $\text{Mo}_2\text{C}$  catalyst compared to

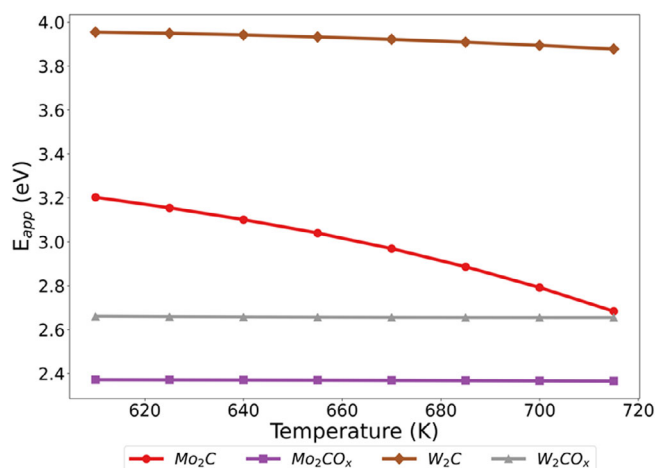


Figure 5. Apparent activation energy as a function of temperature.

$\text{W}_2\text{C}$  catalyst can be attributed to the ability of  $\text{Mo}_2\text{C}$  to partially oxidize (to form oxycarbide) their surface during the reaction, as revealed from the surface coverages (Figure 4A).

## 2.8. Degree of Rate Control (DRC) Analysis

DRC analysis reveals that, in all the cases, multiple elementary steps significantly contribute to the overall rate of the butyric acid HDO reaction (Figure 6). However, there is one elementary step, that is, butanol dissociation ( $\text{C}_4\text{H}_9\text{OH}^* \rightarrow \text{C}_4\text{H}_9^* + \text{OH}^*$ ), which features in all the catalysts studied (TS6 in Figures 2 and 3). These results indicated that butanol dissociation is one of the crucial steps in butyric acid HDO, irrespective of the

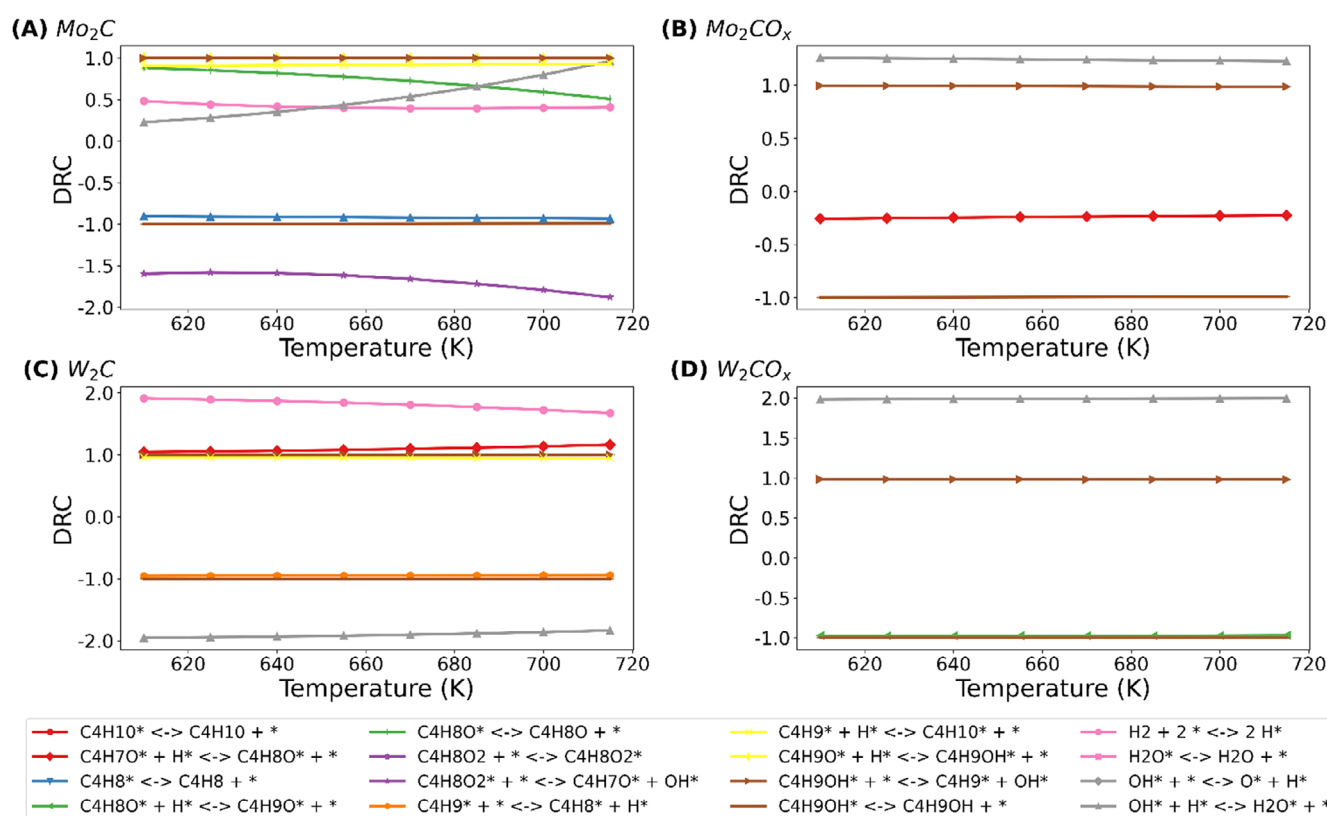


Figure 6. DRC coefficient as a function of temperature. Only the elementary steps with coefficients > 0.2 are shown in the plots.

catalyst, which can serve as a reaction descriptor for HDO activity examination. This is in line with the previous HDO studies, where C—OH activation was found to be the rate-determining step.<sup>[16,32,33]</sup> However, it is important to mention that the other rate-controlling elementary steps could also be considered for further optimization of these catalysts. For instance, the water formation is very difficult on TMOs, and hence the  $\text{OH}^*$  groups block the active sites; therefore, facilitating water formation on these surfaces could enhance the overall activity of the catalysts. Another interesting thing to notice is the difficulty of the hydrogenation steps in TMCs, possibly hinting toward scarcity of  $\text{H}^*$  on the surface, as a result of easy water formation on TMCs compared to TMOs. While water formation is easier on TMCs compared to TMOs, the desorption of water molecules is still a challenge and possibly blocks the active sites. These insights could be used for optimization of these catalysts, by means of heteroatom doping, and vacancy formation. It is worth noting that here the desorption steps are not considered crucial as DFT-D3BJ is known to overestimate the long-range weak interactions,<sup>[34]</sup> resulting in larger DRC coefficients.

## 2.9. Selectivity Analysis

For all the calculated HDO reaction mechanisms, we checked their selectivity toward alkene ( $\text{C}_4\text{H}_8$ ), and alkane ( $\text{C}_4\text{H}_{10}$ ) products. From Figure 7, it is clear that carbides ( $\text{Mo}_2\text{C}$ ,  $\text{W}_2\text{C}$ ) are selective toward unsaturated hydrocarbons, that is,  $\text{C}_4\text{H}_8$ . In contrast, the oxycarbides ( $\text{Mo}_2\text{CO}_x$ ,  $\text{W}_2\text{CO}_x$ ) are selective toward

saturated hydrocarbons, that is,  $\text{C}_4\text{H}_{10}$ . This selectivity of TMCs toward alkene products is in line with previous experimental and theoretical studies.<sup>[8,9,35]</sup> As highlighted in the DRC analysis, the availability of excess  $\text{H}^*$  on the oxycarbide surfaces facilitates the hydrogenation reaction of  $\text{C}_4\text{H}_8$  to  $\text{C}_4\text{H}_{10}$ . These observations are similar to the observations by Khoshooei et al. where they show that the activity of  $\alpha\text{-Mo}_2\text{C}$  for reverse water gas shift increases as a function of  $\text{H}_2/\text{CO}_2$  ratio, that is, in the presence of excess  $\text{H}^*$ .<sup>[36]</sup>

## 3. Conclusions

In this work, we compared the reactivity of TMOs ( $\text{Mo}_2\text{CO}_x$ ,  $\text{W}_2\text{CO}_x$ ) with TMCs ( $\text{Mo}_2\text{C}$ ,  $\text{W}_2\text{C}$ ) for the HDO reaction of *n*-butyric acid to *n*-butane. It is identified that  $\text{Mo}_2\text{CO}_x$  is the most active and selective catalyst for this HDO reaction, followed closely by  $\text{W}_2\text{CO}_x$ . The  $\text{O}^*$  domains on the surface enhance the activity of these catalysts by easing the dissociation of the C—O bond and promoting the hydrogenation reactions due to excess  $\text{H}^*$  on the surface, as compared to the pure TMCs. These insights imply the importance of controlling the carburization extent of the TMC catalysts to achieve high HDO activity and selectivity.

## 4. Computational Details

All DFT calculations have been performed using the Vienna Ab Initio Simulation Package (VASP).<sup>[37,38]</sup> The generalized

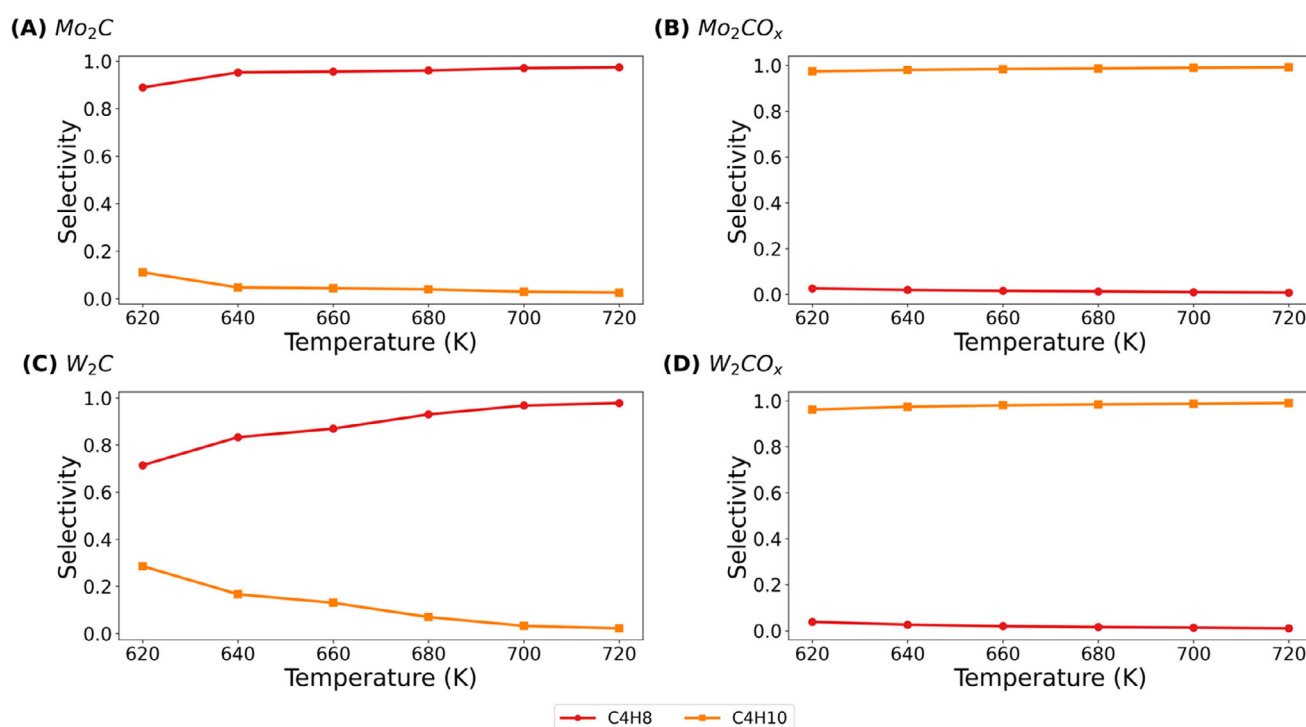


Figure 7. Selectivity toward alkane and alkene as a function of temperature. The y-axis is normalized for comparison.

gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional was used for the exchange–correlation energy.<sup>[39,40]</sup> The kinetic energy cut-off of the plane wave basis set was set to 500 eV. The convergence criterion for energy calculation and structure relaxation was set to a self-consistent field threshold of  $10^{-5}$  eV, and a maximum force threshold of 0.05 eV/Å.  $\Gamma$ -centered k-meshes of the size of  $6 \times 6 \times 6$  and  $2 \times 2 \times 1$  were used for sampling the Brillouin zone in the case of bulk and slab models, respectively. Gaussian-type smearing with a width of 0.05 eV was applied for the electronic energy density of states. For identifying the transition states, the climbing-image nudged elastic band (CI-NEB) method was used, and frequency analysis was performed to confirm that there was only one imaginary frequency along the reaction coordinate.<sup>[41]</sup> For CI-NEB calculations, the maximum force threshold of 0.10 eV/Å was implemented. Dipole corrections were applied in the vacuum (z) direction. The van der Waals interactions were described by the DFT-D3BJ method developed by Grimme et al.<sup>[42,43]</sup> It is important to highlight that DFT-D3 is known to overestimate the binding energies of the reactants on the solid surface,<sup>[34]</sup> and therefore yields a larger desorption barrier for the reactant and product.

The bulk structures of orthorhombic Mo<sub>2</sub>C (mp-1552) and orthorhombic W<sub>2</sub>C (mp-2034) were obtained from the Materials Project website and were fully relaxed. The obtained lattice parameters for Mo<sub>2</sub>C:  $a = 4.75$  Å,  $b = 5.23$  Å,  $c = 6.05$  Å (from experiments:  $a = 4.74$  Å,  $b = 5.21$  Å,  $c = 6.03$  Å),<sup>27</sup> and for W<sub>2</sub>C:  $a = 4.75$  Å,  $b = 5.24$  Å,  $c = 6.09$  Å (from experiments:  $a = 4.73$  Å,  $b = 5.20$  Å,  $c = 6.01$  Å)<sup>[28]</sup> were in good agreement with the experimentally reported values. From the optimized bulk(s), we cleaved a stable (101) surface and built a unit cell with nine

atomic layers thickness (three stoichiometric layers), as shown in Figure 1. Additionally, the carbon atoms in the top layer of TMCs were replaced by oxygen to create the TMOC surfaces, as in the study by Ammal et al.<sup>[21]</sup> For all the slab models, a vacuum distance of 15 Å was introduced in the z-direction to minimize interaction with the periodic images. After relaxing the atoms in the unit cell, we created a supercell of the size  $2 \times 3 \times 1$ , which was deemed to be a big enough surface for the HDO reaction. The bottom six atomic layers of the supercell were fixed to reduce the computational cost of the calculations and to mimic the bulk.

The adsorption energies ( $E_{\text{ads}}$ ), reaction energies ( $\Delta E$ ), and activation barriers ( $E_{\text{a}}$ ) were calculated as follows.

$$E_{\text{ads}} = E_{\text{slab+reactant}} - E_{\text{slab}} - E_{\text{reactant}} \quad (1)$$

$$\Delta E = E_{\text{product}} - E_{\text{reactant}} \quad (2)$$

$$E_{\text{a}} = E_{\text{transition state}} - E_{\text{reactant}} \quad (3)$$

Here,  $E_{\text{slab+reactant}}$  is the total energy of the slab with a reactant adsorbed on it,  $E_{\text{slab}}$  is the total energy of the clean slab,  $E_{\text{reactant}}$  and  $E_{\text{product}}$  are the total energies of the reactant and product of each elementary reaction step, and  $E_{\text{transition state}}$  is the total energy of the transition state (TS). The zero-point energies were corrected for all the elementary steps. The entropic contributions were considered for all the adsorption and desorption steps of gas-phase molecules.

Ab initio molecular dynamics (AIMD) simulations were performed using the CP2K-6.3 package.<sup>[44,45]</sup> An MD step length of

0.5 fs was used. The systems were allowed to evolve for 5 ps in the NVT canonical ensemble, equilibrated using a canonical sampling through velocity rescaling (CSVR) thermostat set at 623 K. The force field was computed using the PBE functional, and Grimme's DFT-D3BJ method was used to describe the vdW interactions.<sup>[42,43]</sup> Atoms were described using double- $\zeta$  molecularly optimized (MOLOPT) gaussian basis sets<sup>[46,47]</sup> and associated Goedecker–Teter–Hutter pseudopotential.<sup>[48]</sup>

The MKMCXX package was used for the microkinetic modelling (MKM) simulations.<sup>[49]</sup> MKM is a tool used to identify the critical intermediates and rate-determining elementary reactions. The chemo-kinetic network was modeled using a set of ordinary differential equations involving rate constants, surface coverages, and partial pressures of gas-phase species ( $\text{C}_4\text{H}_8\text{O}_2:\text{H}_2$  as 1:3),  $p_{\text{H}_2} = 30$  bar, and reaction temperature of 623 K. Time-integration of the differential equations was conducted using the linear multistep backward differential formula method with a relative and absolute tolerance of  $10^{-8}$ .

The rate constant ( $k$ ) of an elementary reaction step is given as:

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} e^{(-\Delta E_a/k_B T)} \quad (4)$$

where  $Q^\ddagger$  and  $Q$  are the partition functions of the activated complex and its corresponding initial state, respectively, and  $\Delta E_a$  is the activation energy.

To identify the steps that control the butyric acid consumption rate and the product distribution, we performed the degree of rate control (DRC) analysis, as developed by Kozuch and Shaik,<sup>[50,51]</sup> and popularized by Campbell.<sup>[31]</sup>

The DRC coefficient is defined as:

$$X_{RC,i} = \left( \frac{\partial \ln r_i}{\partial \ln k_i} \right)_{k_{j \neq i}, K_j} \quad (5)$$

where  $X_{RC,i}$  is the degree of rate control coefficient,  $r_i$  the overall reaction rate,  $k_i$  the reaction rate constant for elementary reaction step  $i$  and  $K_i$  the equilibrium constant of elementary reaction step  $i$ .

While the sensitivity analysis was performed using the following equation:

$$\varepsilon_{i,c} = \left( \frac{\partial \eta_c}{\partial \ln k_i} \right)_{k_{j \neq i}, K_j} \quad (6)$$

where  $\varepsilon_{i,c}$  is the degree of selectivity coefficient (DSC) of compound  $c$  due to a change in elementary reaction step  $i$  and  $\eta_c$  is the selectivity of compound  $c$ .

Once the DRC coefficients are known, we can calculate the DSC using the following equation.

$$\varepsilon_{i,c} = \eta_c (X_{C,i} - X_{R,i}) \quad (7)$$

In other words, the DSC is the DRC using the rate of the compound you are interested in minus the DRC using the rate of the overall reaction (i.e., of a specific reactant), multiplied by the selectivity of the compound of interest. A positive DSC indicates

that the selectivity of this compound will increase when the barrier of the corresponding elementary reaction step is lowered, whereas a negative value indicates that the selectivity decreases if the barrier is lowered.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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