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# Multiscale modelling of CO<sub>2</sub> hydrogenation of TiO<sub>2</sub>-supported Ni<sub>8</sub> clusters: on the influence of anatase and rutile polymorphs†

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The selection of TiO<sub>2</sub> phase, whether anatase or rutile, for supporting small Ni clusters significantly influences the activity and selectivity in CO<sub>2</sub> hydrogenation to methane. To model and understand these variances, we developed a hierarchical multiscale catalytic model. Utilizing a hybrid approach combining genetic algorithms and density functional theory, we identified the putative global minimum structures of Ni<sub>8</sub> clusters supported on anatase (Ni<sub>8</sub>/TiO<sub>2</sub>-a) and rutile (Ni<sub>8</sub>/TiO<sub>2</sub>-r), which are morphologically distinct. Microkinetics simulations based on the energetics derived from DFT calculations over these distinct clusters reveal the mechanism of CO<sub>2</sub> hydrogenation to CO, CH<sub>4</sub> and CH<sub>3</sub>OH. On both Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r, CH<sub>4</sub> is the main product at low temperature while a shift to CO occurs with increasing temperature. In comparison to Ni<sub>8</sub>/TiO<sub>2</sub>-r, Ni<sub>8</sub>/TiO<sub>2</sub>-a exhibits a higher activity and keeps a higher selectivity towards CH<sub>4</sub> with increasing temperature. Using a sensitivity analysis, we identify the steps responsible for the observed selectivity difference and rationalize the observed barrier differences for these steps between the different clusters by means of detailed electronic structure analysis.

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## 1. Introduction

In recent decades, the escalating levels of atmospheric carbon dioxide (CO<sub>2</sub>) contribute significantly to rising global temperatures, sea-level rise, altered weather patterns, and various ecological disruptions. To mitigate these adverse effects and transition towards a more sustainable and carbon-neutral future, innovative approaches and technologies capable of reducing CO<sub>2</sub> emissions at scale are required.<sup>1–5</sup> Sustainably produced hydrogen, for example from excess wind and solar power, can be utilized to convert CO<sub>2</sub> to CH<sub>4</sub> in the so-called power-to-gas concept.<sup>6–8</sup> An important benefit of CH<sub>4</sub> is that existing infrastructure for storage and transport can be repurposed.<sup>6,9</sup>

For the practical implementation of CO<sub>2</sub> hydrogenation to CH<sub>4</sub>, catalysts are essential to ensure both high reaction rates and selectivity towards the desired product. While methanation catalysts have been extensively studied, Ru stands out for its superior performance among investigated transition metals.<sup>10,11</sup> However, the widespread industrial application of Ru catalysts

is hindered by its relatively high cost. In contrast, Co and Ni also demonstrate high conversion rates in CO<sub>2</sub> methanation, with Ni being the preferred choice for industrial applications, as it is the cheaper of the two metals.<sup>12–14</sup>

The activity of supported transition metal catalysts is affected by many factors, with the size of the nanoparticles being a dominant one, strongly affecting the abundance of specific surface atom arrangements relevant to dissociation and association reactions below 10 nm.<sup>15</sup> The effect of nanoparticle size on the activity and selectivity of CO<sub>2</sub> hydrogenation to CO and CH<sub>4</sub> remains a topic of intense debate. Two dominant trends can be identified in the literature. Some studies show an increased surface-normalized CO<sub>2</sub> conversion with increasing particle size,<sup>16–21</sup> while others find an optimum.<sup>22–24</sup> In a recent study of Simons *et al.*, it was found that Ni-catalyzed CO<sub>2</sub> methanation uses two different types of active sites, one for reverse-water-gas-shift (RWGS) reaction yielding intermediary CO and another type of site for CO conversion to methane. While RWGS is structure-independent, the activity of CO methanation shows strong structure-dependence caused by the particle size dictating the abundance of this latter type of active site.<sup>25</sup>

In addition to nanoparticle size, the support material can influence the morphology of the nanoparticles. Apart from the wetting properties of the support affecting the nanoparticle, the surface structure of the support also has an epitaxial effect that influences nanoparticle morphology by favoring specific

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alignments at the support–nanoparticle interface.<sup>26–29</sup> A notable example is found when using TiO<sub>2</sub> as a support material, which exists in three primary crystalline forms, being anatase, rutile and brookite. CO<sub>2</sub> methanation catalyzed by TiO<sub>2</sub>-supported nanoparticles show different activity and selectivity trends based on the phase of TiO<sub>2</sub>.<sup>30–33</sup> Li *et al.* showed that for similarly sized Co nanoparticles (~20 nm), the anatase-supported particles mainly produce CO under CO<sub>2</sub> hydrogenation conditions, while the rutile-supported counterpart exhibits high methane selectivity.<sup>30</sup> Wang *et al.* reported a similar effect for small Ru nanoparticles (~2–3 nm), where the rutile phase is significantly more active and selective towards CH<sub>4</sub> than the anatase phase. This enhanced selectivity is assigned to the formation of a favorable overlayer structure guided by the interfacial compatibility between the RuO<sub>2</sub> precursor phase and rutile, prior to reduction. In contrast, on anatase only small nanoparticles are formed.<sup>32</sup> Likewise, the works of Lin *et al.* and Messou *et al.* observe for similarly sized Ni nanoparticles (~30 nm) an increased activity and selectivity towards CH<sub>4</sub> for the rutile phase over the anatase phase in CO<sub>2</sub> hydrogenation. The increased activity is assigned to the rutile phase giving rise to Ni nanoparticles that portray facile CO dissociation and H<sub>2</sub> activation.<sup>31,33</sup>

Clearly, the choice of TiO<sub>2</sub> phase, whether anatase or rutile, has a strong impact on the catalytic activity, even when the nanoparticles are roughly the same size. Different support materials, their phases and surface termination determine the metal–support interaction strength and thus modulate particle sizes invoking known structure sensitivity patterns. When nanoparticle sizes remain comparable between different support structures, yet a different kinetic response is observed, this is a strong indicator that the support influences the particle shape. Computational catalysis can aid in understanding these effects, yet the scale of these systems remains still prohibitively large for detailed electronic structure calculations. One way to tackle this is by means of DFT-based force fields, as performed earlier by us for both unsupported Co nanoparticles<sup>26</sup> as well as Co nanoparticles on a model support material.<sup>34</sup> In this work, rather than producing such a force field, the system is made computationally accessible by focusing on small Ni clusters. Small Ni clusters provide an excellent model system to study active site configurations that are guided by the alignment of the support substructure.

To understand and characterize how support effects can influence the activity and selectivity in CO<sub>2</sub> hydrogenation to methane for small clusters, we construct a multiscale model for Ni<sub>8</sub> clusters supported on rutile and anatase. Although experimentally always a range of particle size distributions is observed, these small Ni<sub>8</sub> clusters are representative for particle sizes below 1 nm. By means of a DFT-based genetic algorithm in conjunction with machine learning, we explore the configuration space of TiO<sub>2</sub>-supported Ni<sub>8</sub> clusters and identify the putative global minimum configuration. Next, the kinetic pathways for CO<sub>2</sub> hydrogenation to CH<sub>4</sub> are calculated. By means of microkinetics simulations, we found that Ni<sub>8</sub>/TiO<sub>2</sub>-anatase in comparison to Ni<sub>8</sub>/TiO<sub>2</sub>-rutile exhibits a much

higher activity while also portraying a higher selectivity to CH<sub>4</sub> with increasing temperature. Using a sensitivity analysis, we identified that the preferred manner of C–O bond scission – hydrogen-assisted pathway *via* HCO\* for Ni<sub>8</sub>/TiO<sub>2</sub>-anatase, while in a direct fashion for Ni<sub>8</sub>/TiO<sub>2</sub>-rutile – dictates the observed activity and selectivity differences. These differences are caused by the specific topology of the active site dictated by the alignment of Ni atoms with the support structure. By means of a crystal orbital Hamilton population analysis, the difference in barrier for CO dissociation is rationalized. This study adds to our understanding by which mechanism the catalyst support can modulate the catalytic reaction.

## 2. Methods

### 2.1 DFT calculations

All density functional theory (DFT) calculations were performed using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional<sup>35</sup> as implemented in the Vienna *ab initio* simulation package (VASP) software.<sup>36,37</sup> All DFT calculations were conducted with spin-polarization taken into account. The interaction of the core-electrons and nucleus was described with the Projector Augmented Wave (PAW) method.<sup>38–40</sup> The cut-off energy was set to 400 eV. The Brillouin zone was sampled using a 1 × 1 × 1 grid. Gaussian smearing with a width of 0.05 eV determined partial occupancies for each orbital. Ionic convergence was achieved when the forces were smaller than 0.05 eV Å<sup>-1</sup> for each atom in each Cartesian direction. A Van-der-Waals correction was added to our calculation using the DFT-D3 method with the Becke–Johnson damping function.<sup>41,42</sup> Climbing image nudged elastic band (CI-NEB) was employed to investigate the transition pathway.<sup>43,44</sup> The transition state was optimized using a quasi-Newton algorithm and the optimized geometry was examined by vibrational mode analysis. It was verified that all transition states have a single imaginary mode in the direction of the reaction coordinate. We employed a finite difference approach to construct the Hessian matrix for frequency analysis by perturbing the atomic positions by 0.01 Å in each Cartesian direction. Furthermore, the vibrational mode analysis was used to construct zero-point energy corrections.

### 2.2 Structural models

For anatase and rutile TiO<sub>2</sub>, the periodically repeated (101) and (110) surface terminations were employed as supports for Ni<sub>8</sub> clusters, as these surfaces are known to be the most thermodynamically stable for their respective phases.<sup>45,46</sup> Ni<sub>8</sub> clusters deposited on (101) surface of TiO<sub>2</sub> anatase and (110) surface of TiO<sub>2</sub> rutile are denoted as Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r, respectively. We specifically selected Ni<sub>8</sub> clusters because they are large enough to potentially support step-edge configurations, which are known to promote C–O bond scission.<sup>47</sup> However, this does not guarantee that these active site patterns are thermodynamically favorable, as the support interface also plays a crucial role. Nevertheless, choosing smaller cluster sizes would *a priori* prevent studying such sites.



The lattice parameters of TiO<sub>2</sub>-a and TiO<sub>2</sub>-r bulks were optimized and found to be 3.816 Å × 3.816 Å × 9.539 Å and 4.650 Å × 4.650 Å × 2.966 Å, respectively. These optimized lattice parameters are in good agreement with the values obtained from experimental results.<sup>48,49</sup> For TiO<sub>2</sub>-a, a 1 × 3 (101) surface termination with dimensions of 10.42 Å × 11.46 Å was constructed. Its slab model hosts three O–Ti–O layers with the bottom layer fixed while the top two layers are allowed to relax.<sup>50</sup> For Ni<sub>8</sub>/TiO<sub>2</sub>-r, a 5 × 2 (110) surface termination with dimensions of 14.85 Å × 13.18 Å was constructed. The corresponding slab model has four O–Ti–O layers. The bottom layer was fixed while the top three layers were allowed to perturb. To avoid the spurious interaction of neighboring supercells in the z-direction, the TiO<sub>2</sub>-a and TiO<sub>2</sub>-r super cells have a vacuum space of at least 15 Å. A depiction of the supercells is given in the ESI† in Fig. S1.

### 2.3 Genetic algorithm

In order to search for the putative global minimum structure of Ni<sub>8</sub> clusters deposited on the anatase (101) and rutile (110) surface of TiO<sub>2</sub>, a GA-DFT algorithm based on the approach as described by Hammer *et al.* was employed.<sup>51</sup> In this approach, an ensemble of cluster configurations is procedurally generated and the stability of these clusters on the surface is assessed by DFT calculations. To efficiently probe the configuration space of cluster configurations, a genetic algorithm method is used wherein new cluster configurations are generated by a sequence of operations including translations, rotations, atomic migrations and mixing of clusters. For each generation, at least 12 candidates are generated to form the next generation. To enhance the diversity of the population, approximately 30% to 50% of the structures are mutated. Each cluster is subjected to a geometry optimization in a conventional DFT simulation and based on the energies of the clusters they are ranked in terms of stability. New generations of clusters are derived from an older generation using stability and similarity metrics. This yields a strong (*i.e.* containing many stable structures) yet sufficiently diverse population between all iterations. The algorithm is considered to be converged when no new more stable configurations are found for a number of generations, typically between 5–10. Details of the GA-DFT procedure can be found in the earlier work of Chang *et al.*<sup>52</sup>

To assess the similarity of the clusters and identify common shapes, an unsupervised non-linear dimensionality reduction was conducted *via* the *t*-distributed stochastic neighbor embedding (*t*-SNE) method as implemented in the sklearn Python library.<sup>53,54</sup> The dimensionality reduction is applied to a  $N \times N$  square distance metric matrix  $M$  with  $N$  being the number of clusters. Each element in  $M$  corresponds to the minimized Hilbert–Schmidt norm<sup>55</sup> of the distance-difference matrix between two clusters. The minimized Hilbert–Schmidt norm is constructed by first constructing an atomic distance matrix  $R$  for each cluster.

$$R = \begin{pmatrix} 0 & \dots & r_{ij} \\ \vdots & \ddots & \vdots \\ r_{ji} & \dots & 0 \end{pmatrix}, \quad (1)$$

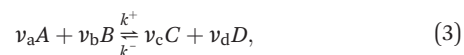
wherein  $r_{ij}$  is the Euclidean distance between atom  $i$  and atom  $j$  in a cluster. As such, the matrix  $R$  is symmetric and has zeros on its diagonal. Given two atomic distance matrices  $R_k$  and  $R_l$  for clusters  $k$  and  $l$ , a similarity metric  $S_{kl}$  can be constructed by evaluating

$$S_{kl} = \sqrt{\sum_{ij} (r_{ij}^{(k)} - r_{ij}^{(l)})^2}. \quad (2)$$

Although the distance matrix  $R$  is translationally and rotationally invariant, it is not permutationally invariant and as such, the value of  $S_{kl}$  depends on the specific indexing of the atoms. Consequently, the value of  $S_{kl}$  needs to be minimized by considering all possible permutations of the atomic indices for one of the clusters. Given the small number of atoms in the clusters, it is possible to employ a brute force approach wherein all  $8! = 40320$  permutations were explicitly considered. The lowest value found, *i.e.*  $S_{kl,\min}$ , is then used as the elements to construct  $M$ . For the construction of  $M$ , we used the in-house developed program Bramble which employs a GPU-accelerated procedure to evaluate all permutations.<sup>56</sup>

### 2.4 Microkinetics simulations

Microkinetics simulations based on DFT-derived reaction networks were conducted to determine the catalytic performance of Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r for CO<sub>2</sub> hydrogenation. All microkinetics simulations were performed using the in-house developed MKMCXX program.<sup>57,58</sup> For each elementary reaction step in the chemokinetic network as given by



a corresponding rate expression, *i.e.* an ordinary differential equation in time, can be constructed by

$$r_A = -\frac{d[A]}{dt} = v_a (k^+ [A]^{v_a} [B]^{v_b} - k^- [C]^{v_c} [D]^{v_d}) \quad (4)$$

Herein,  $v_X$  is the stoichiometric coefficient of component  $X$  and  $k^+$  and  $k^-$  are the rate constants for the forward and backward reaction, respectively. From harmonic transition state theory, the reaction rate constants are calculated by the Eyring equation

$$k = \frac{k_B T f_{\text{TS}}^\#}{h f_{\text{IS}}^\#} \exp\left(-\frac{\Delta E_a}{k_B T}\right) \quad (5)$$

wherein  $h$  is the Planck constant,  $\Delta E_a$  the activation energy,  $k_B$  the Boltzmann constant,  $T$  the temperature, and finally  $f_{\text{TS}}^\#$  and  $f_{\text{IS}}^\#$  are the partition functions of the transition state and the initial state, respectively.

For the adsorption steps, it is assumed that the adsorbing molecule loses one of the translational degrees of freedom with respect to the initial state. The rate constant for



adsorption is then determined by the rate of surface impingement of gas-phase molecules for non-activated molecular adsorption and is given by<sup>59</sup>

$$k_{\text{ads}} = \frac{PA}{\sqrt{2\pi mk_{\text{B}}T}}, \quad (6)$$

wherein  $P$  corresponds to the partial pressure of the adsorbate in the gas phase,  $A$  the effective surface area of the adsorption site, and  $m$  the mass of the adsorbate.

Considering the reversibility of the adsorption step, the molecule regains all its rotational degrees of freedom (*i.e.* three degrees of freedom for non-linear molecules and two degrees of freedom for linear molecules) and two translational degrees of freedom in the desorption step. Therefore, the desorption rate is given by

$$k_{\text{des}} = \frac{k_{\text{B}}T}{h} \frac{q_{\text{vib,gas}} q_{\text{rot,gas}} q_{\text{tran2D,gas}}}{q_{\text{vib,ads}}} \exp\left(\frac{\Delta E_{\text{ads}}}{k_{\text{B}}T}\right) \quad (7)$$

wherein  $\Delta E_{\text{ads}}$  is the adsorption energy.  $q_{\text{vib,gas}}$ ,  $q_{\text{rot,gas}}$  and  $q_{\text{tran2D,gas}}$  represent the vibrational, rotational and two-dimensional translation partition function of a molecule in gas phases, respectively.  $q_{\text{vib,ads}}$  refers to the vibrational partition function of the molecule upon adsorption.

In our simulations, the initial gas phase contained a mixture of  $\text{CO}_2$  and  $\text{H}_2$  in a 1:4 ratio at a total pressure of 1 atm, in line with the conditions used in the experiment.<sup>60</sup> To identify the elementary reaction steps that control the overall rate of  $\text{CO}_2$  consumption, Campbell's degree of rate control analysis was employed.<sup>61</sup>

## 3. Results and discussions

### 3.1 $\text{Ni}_8$ clusters supported on anatase and rutile $\text{TiO}_2$

To find the most stable structures for  $\text{Ni}_8$  clusters supported on anatase and rutile  $\text{TiO}_2$ , a GA-DFT algorithm was employed which produced 244 and 104 candidate structures for the anatase and rutile systems, respectively. The candidates were ranked based on the total energy of the system. The 10 most stable structures for anatase and rutile  $\text{TiO}_2$  are given in Fig. S2 and S4,<sup>†</sup> respectively. To investigate whether there are multiple cluster configurations that are topologically distinct yet portray a similar stability on the surface, a similarity analysis was conducted by calculating the minimized Hilbert–Schmidt norm between all clusters. Using a non-linear dimensionality reduction based on the  $t$ -SNE method, we could classify all clusters into distinct categories as shown in Fig. 1. Representative cluster configurations for each of these groups are shown in Fig. 1 as well.

The most stable Ni cluster on the anatase  $\text{TiO}_2$  (101) surface, representative of group 1, adopts a bilayer configuration in which 6 Ni atoms are located in the bottom layer forming two fourfold type of adsorption sites on which the two atoms of the top layer are located. The clusters in groups 2–4 exhibit fewer Ni atoms binding to the O atoms of the support and are higher in energy. In Fig. S3,<sup>†</sup> the 9 most similar clusters with respect to the most stable cluster are shown. We can readily observe that

these structures are related to the most stable structure either *via* a rotation or *via* a migration of one or two Ni atoms.

On the rutile  $\text{TiO}_2$  (110) surface, the most stable cluster of  $\text{Ni}_8$  also adopts a bilayer configuration. In contrast to the anatase system, the bottom layer has a triangular shape exposing four threefold adsorption sites. The top layer is constructed by the adsorption of two Ni atoms on two of these threefold adsorption sites. The  $t$ -SNE manifold learning shows that, for this system, also four distinct groups of clusters are found. The most stable configuration belongs to group 1, group 2 shows a different configuration yet similar to group 1 on anatase  $\text{TiO}_2$ (101) with 6 atoms in the bottom layer and two atoms in the top layer. In contrast, groups 3 and 4 show a configuration with 5 atoms in the bottom layer and 3 in the top layer. Groups 2, 3 and 4 are, on average, higher in energy than group 1 as they either lack a strong interaction with the support (groups 3 and 4) or have more undercoordinated metal atoms (group 2).

Furthermore, due to known SMSI effects, we also investigated planar  $\text{Ni}_8$  clusters that optimize the contact area between the  $\text{TiO}_2$ -support and the  $\text{Ni}_8$  cluster. The configurations are shown in Fig. S6 in the ESI.<sup>†</sup> It was found that on both  $\text{TiO}_2$  anatase and rutile, a planar  $\text{Ni}_8$  cluster is less stable than a non-planar cluster by 1.35 eV and 1.06 eV, respectively. As such, we proceeded with evaluating the elementary reaction steps for  $\text{CO}_2$  hydrogenation using non-planar cluster configurations.

### 3.2 Chemical reactivity of $\text{CO}_2$ hydrogenation over $\text{Ni}_8/\text{TiO}_2$ -a and $\text{Ni}_8/\text{TiO}_2$ -r

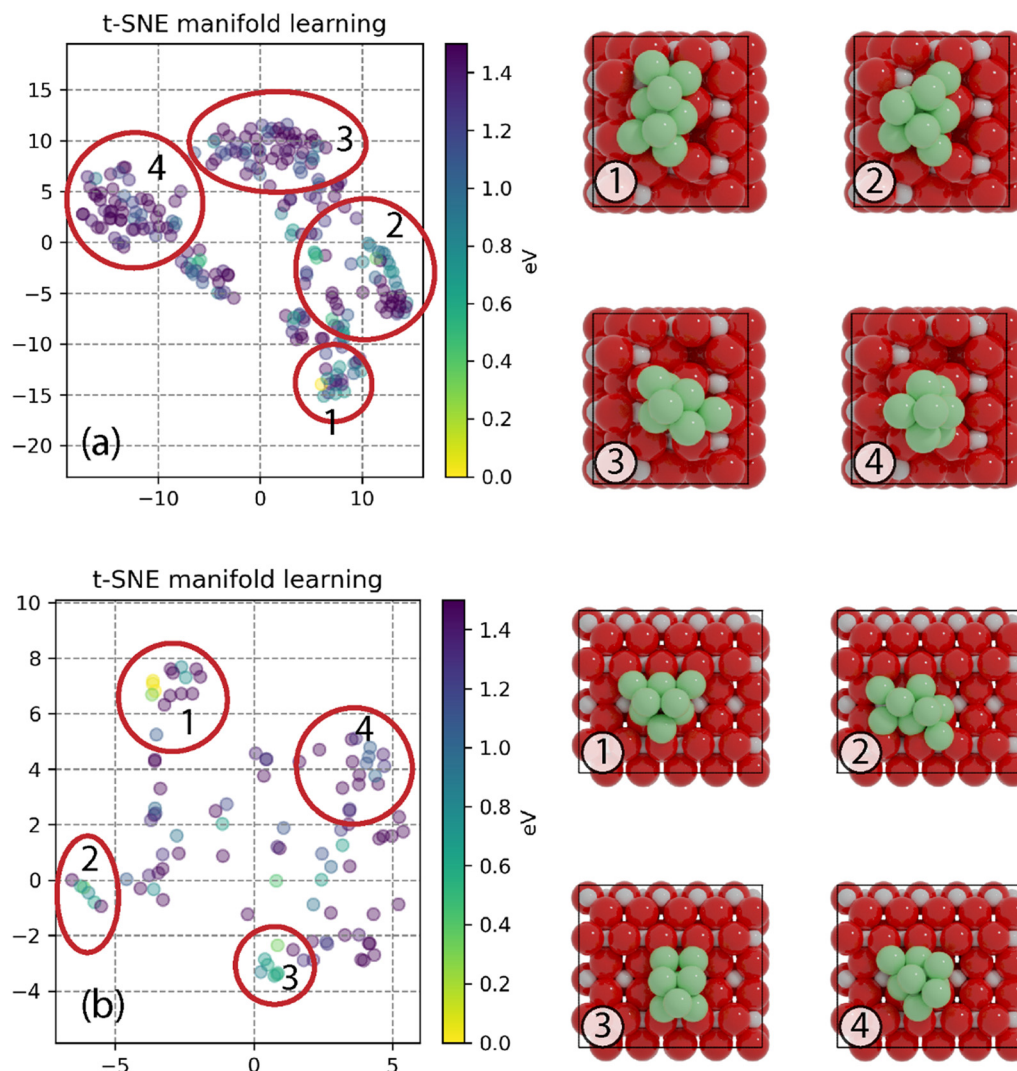
**3.2.1 Adsorption of  $\text{CO}_2$  and  $\text{H}_2$ .** In Fig. 2, the two most stable cluster configurations for anatase and rutile are shown. To label the different types of active sites involved in the mechanism, we employ the following notations:

- $T_i$ : the top site of  $\text{Ni}_i$ .
- $B_{i-j}$ : the bridge site located between  $\text{Ni}_i$  and  $\text{Ni}_j$ .
- $H_{i-j-k}$ : the hollow site that comprises  $\text{Ni}_i$ ,  $\text{Ni}_j$ , and  $\text{Ni}_k$ .
- $F_{i-j-k-l}$ : the four-fold site formed by  $\text{Ni}_i$ ,  $\text{Ni}_j$ ,  $\text{Ni}_k$ , and  $\text{Ni}_l$ .

First, the preferred adsorption configurations of  $\text{CO}_2$  and  $\text{H}_2$  on the various active sites are explored. For  $\text{H}_2$ , we considered both molecular as well as dissociative adsorption. In Fig. 3 and 4, an overview is given of the different adsorption modes and corresponding adsorption energies of  $\text{CO}_2$  and  $\text{H}_2$  on  $\text{Ni}_8/\text{TiO}_2$ -a and  $\text{Ni}_8/\text{TiO}_2$ -r, respectively. From the results in Fig. 3 and 4, it can be seen that dissociative  $\text{H}_2$  adsorption is more exothermic as compared to molecular adsorption and the H atoms preferentially reside at the metal–support interface. The most stable configurations for  $\text{H}_2$  adsorption correspond to adsorption energies of  $\Delta E_{\text{ads}} = -1.23$  eV and  $\Delta E_{\text{ads}} = -1.37$  eV for  $\text{Ni}_8/\text{TiO}_2$ -a and  $\text{Ni}_8/\text{TiO}_2$ -r, respectively. In these configurations,  $\text{H}_2$  is dissociatively adsorbed to form  $2\text{H}^*$ . This process is activated by 0.11 eV and 0.39 eV for  $\text{Ni}_8/\text{TiO}_2$ -a and  $\text{Ni}_8/\text{TiO}_2$ -r, respectively. These results are similar to  $\text{H}_2$  dissociation on a  $\text{Ni}_{13}$  cluster ( $\Delta E_{\text{act}} = 0.21$  eV) and  $\text{Ni}/\text{In}_2\text{O}_3$  ( $\Delta E_{\text{act}} = 0.22$  eV).<sup>62,63</sup> H spillover is



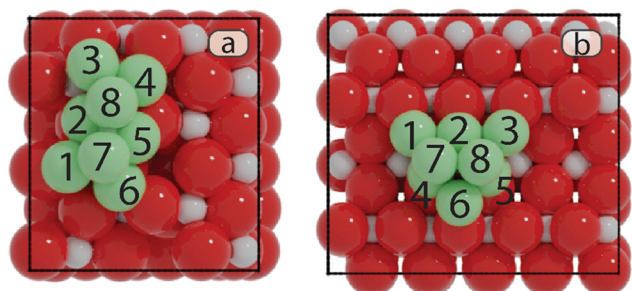




**Fig. 1** t-SNE manifold learning of GA-DFT generated structures of  $\text{Ni}_8/\text{TiO}_2\text{-a}$  (a) and  $\text{Ni}_8/\text{TiO}_2\text{-r}$  (b), with clusters of similar structures encircled and labeled 1–4. Representative structures for each part are displayed on the right of t-SNE figures. Color codes: red: O; light gray: Ti; green: Ni. The energies of all structures relative to the most stable one are shown using a color map. The structure's stability decreases as the color transitions from yellow to purple.

commonly discussed experimentally.<sup>64</sup> Therefore, H spillover is also considered on these two models. As shown in Fig. S7,<sup>†</sup> H spillover occurs with activation energies of  $\Delta E_{\text{act}} = 0.89$  eV and  $\Delta E_{\text{act}} = 1.09$  eV on  $\text{Ni}_8/\text{TiO}_2\text{-a}$  and  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , respectively.

This step is endothermic with reaction energies of  $\Delta E_{\text{R}} = 0.67$  eV and  $\Delta E_{\text{R}} = 0.50$  eV for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  and  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , respectively. Given the endothermic nature of the H spillover reaction and the fact that  $\text{CO}_2$  adsorption takes place on Ni clusters (*vide infra*), H spillover is not further considered in the evaluation of the reaction mechanism. On  $\text{Ni}_8/\text{TiO}_2\text{-a}$ ,  $\text{CO}_2$  adsorption is preferred at the  $\text{B}_{7-8}$  or  $\text{H}_{5-7-8}$  sites, both sites yielding an adsorption energy of  $\Delta E_{\text{ads}} = -0.93$  eV. On  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , the most stable site for  $\text{CO}_2$  adsorption is  $\text{H}_{1-4-7}$  with an adsorption energy of  $\Delta E_{\text{ads}} = -0.70$  eV. Based on the preferred adsorption sites of  $\text{H}_2$  and  $\text{CO}_2$ , we also considered the co-adsorption of  $\text{CO}_2$  and  $\text{H}_2$ . For  $\text{Ni}_8/\text{TiO}_2\text{-a}$  we find a total adsorption energy of  $\Delta E_{\text{ads}} = -2.39$  eV, which is more exothermic than the sum of the individual  $\text{CO}_2$  and  $\text{H}_2$  adsorption energies. In a similar fashion, we find for  $\text{Ni}_8/\text{TiO}_2\text{-r}$  that the co-adsorbed state is more exothermic ( $\Delta E_{\text{ads}} = -2.64$  eV) than the sum of the individual adsorption energies. As these co-adsorbed states represent favorable adsorption



**Fig. 2** The most stable models of  $\text{Ni}_8/\text{TiO}_2\text{-a}$  (a) and  $\text{Ni}_8/\text{TiO}_2\text{-r}$  (b). Color codes: red: O; light gray: Ti; green: Ni. The numbering of Ni atoms corresponds to the active sites as described in the main text.



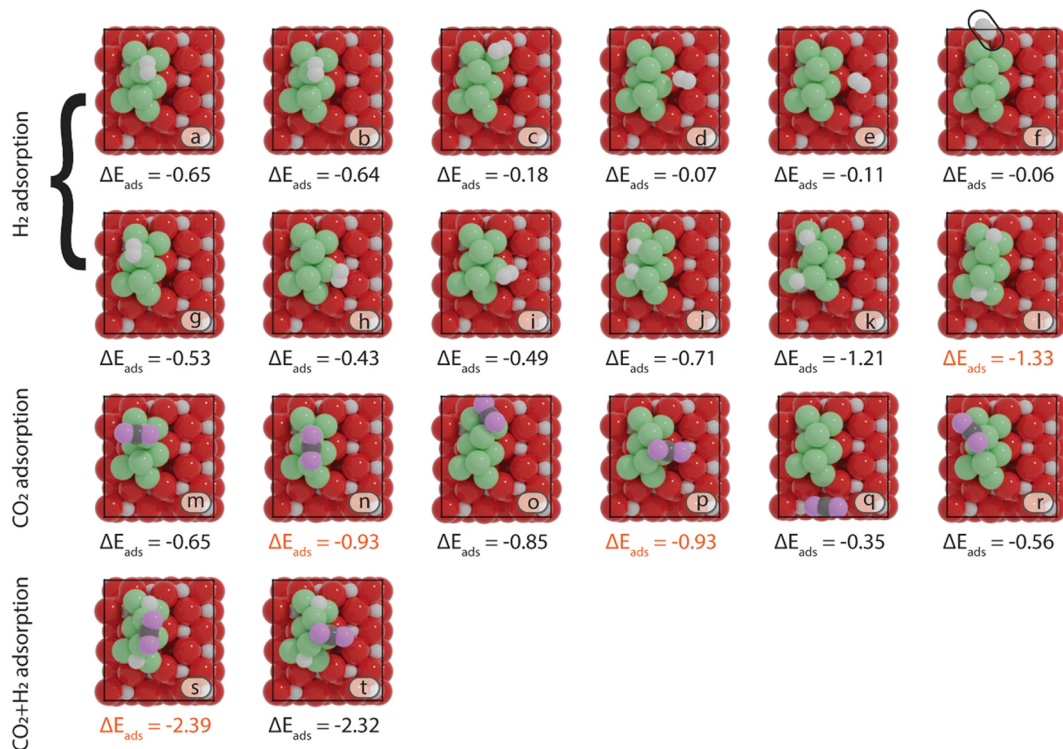


Fig. 3 Configurations of adsorbed  $\text{H}_2$  (a–l),  $\text{CO}_2$  (m–r) and co-adsorption of  $\text{CO}_2$  and  $\text{H}_2$  (s and t) on  $\text{Ni}_8/\text{TiO}_2\text{-a}$ . Color scheme: white: H; pink: O in  $\text{CO}_2$ ; gray: C. A black border has been used to indicate the location of  $\text{H}_2$  in f. The most stable configuration is indicated by the orange labels.

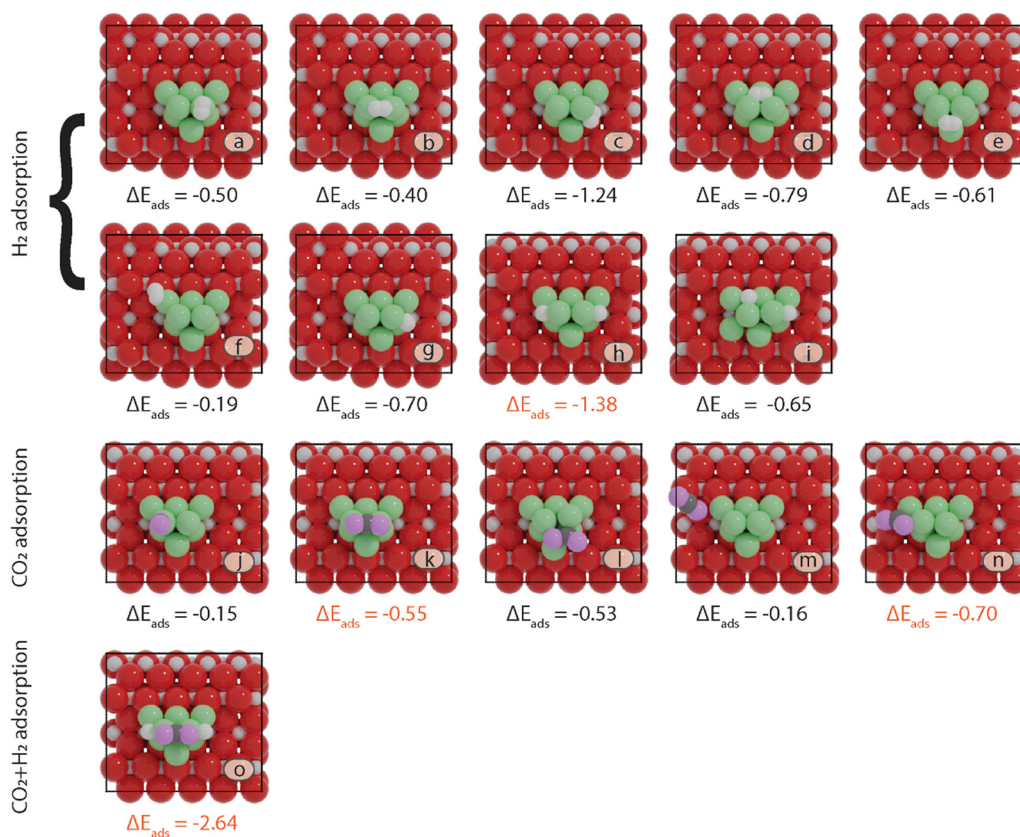


Fig. 4 Configurations of adsorbed  $\text{H}_2$  (a–i),  $\text{CO}_2$  (j–n) and co-adsorption of  $\text{CO}_2$  and  $\text{H}_2$  (o) on  $\text{Ni}_8/\text{TiO}_2\text{-r}$ . Color scheme: white: H; pink: O in  $\text{CO}_2$ ; gray: C. The most stable configuration is indicated by the orange labels.





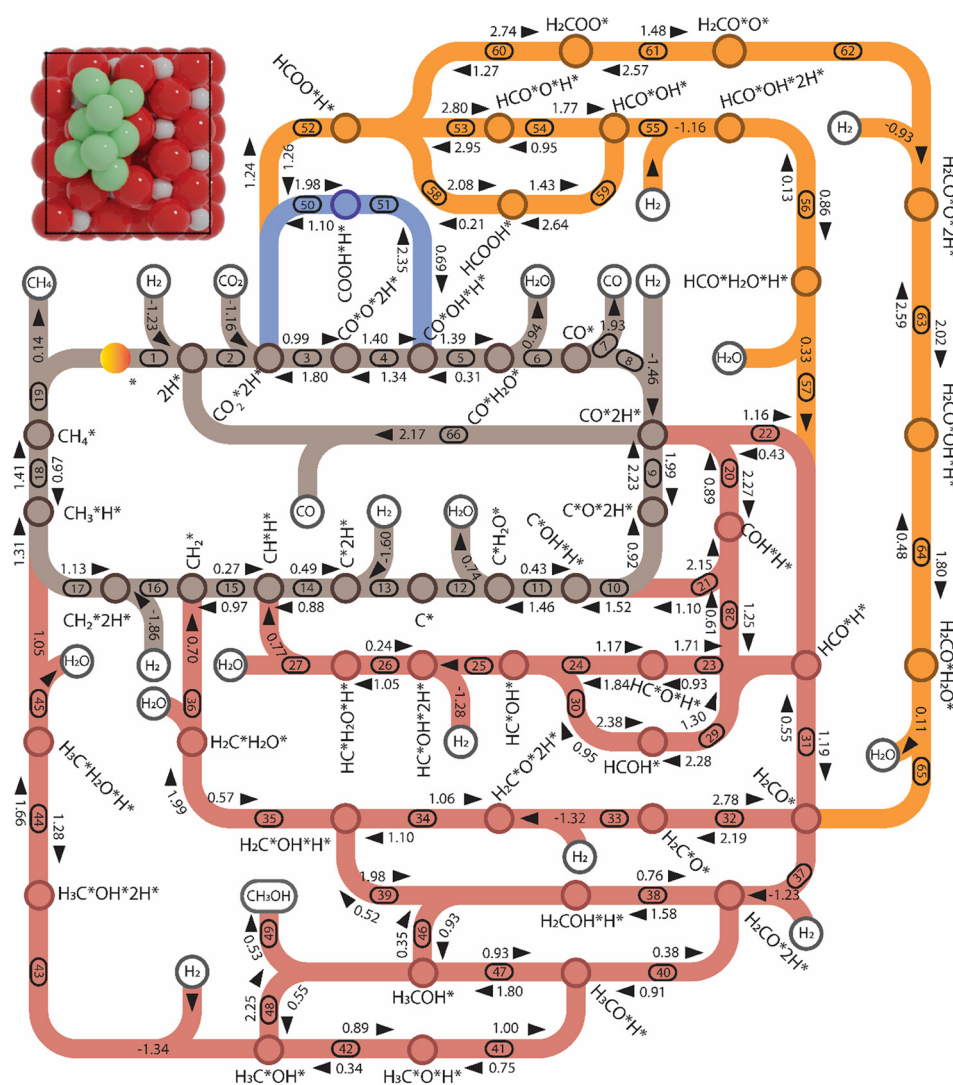
modes, we considered these in the further exploration of the reaction pathways.

**3.2.2 CO<sub>2</sub> hydrogenation.** We computed the reaction energetics of CO<sub>2</sub> hydrogenation to CH<sub>4</sub>, CO, and CH<sub>3</sub>OH on the most stable models identified in the previous section. The networks of elementary reaction steps and their forward and backward activation energies are displayed in Fig. 5 and 6 for Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r, respectively. In this section, we will explore the pathways related to elementary reaction steps involving CH<sub>x</sub> and H<sub>x</sub>CO intermediates in detail. Microkinetic simulations (as discussed later) revealed that the kinetic network associated with H<sub>x</sub>CO<sub>2</sub> intermediates has a minimal impact on the overall reaction mechanism; therefore, this aspect is addressed in Sections S1 and S2 of the ESI.†

### 3.2.2.1 Ni<sub>8</sub>/TiO<sub>2</sub>-a

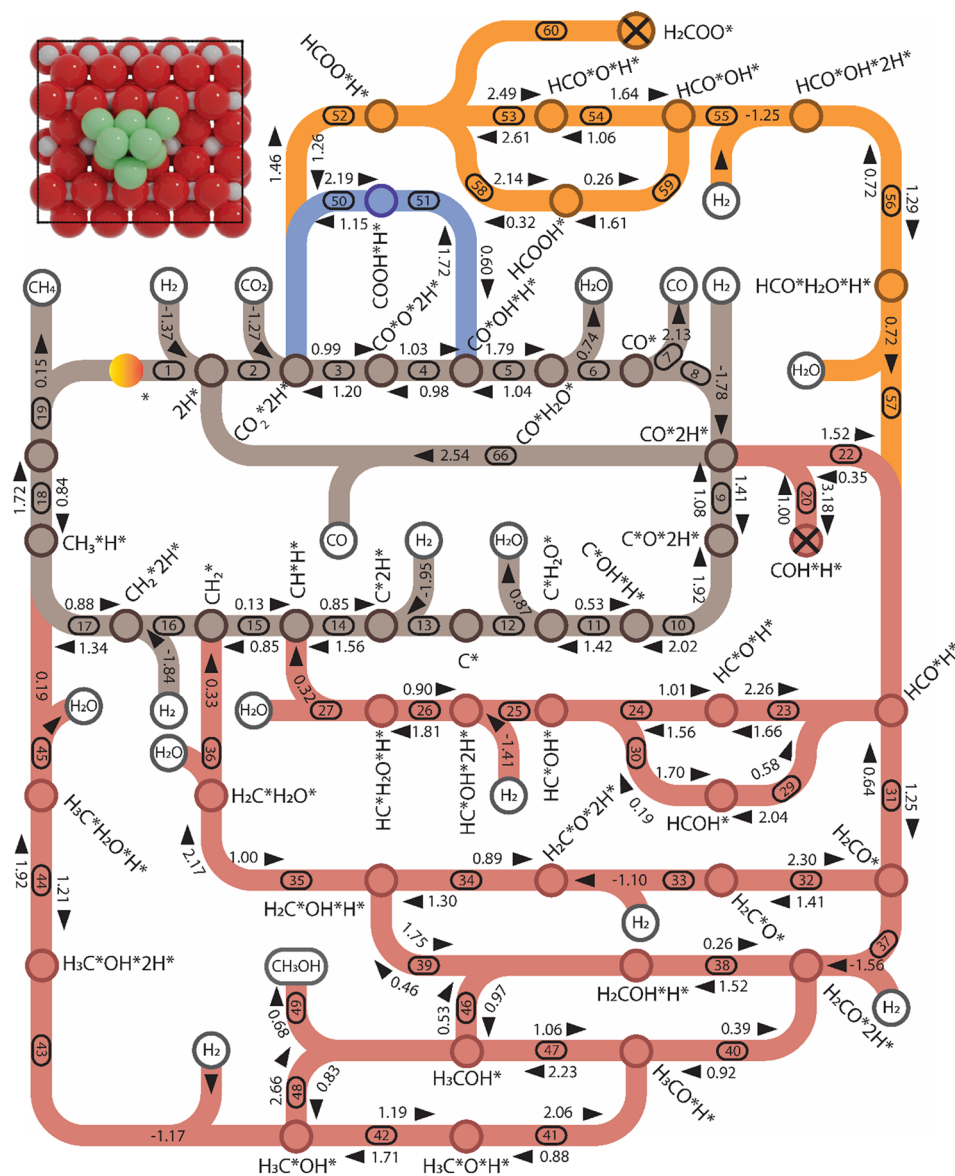
**Pathway involving CH<sub>x</sub> intermediates.** We first discuss the elementary reaction steps among the CH<sub>x</sub> intermediates (R1 to

R19; brown section in Fig. 5) with CH<sub>4</sub> and CO as the main products. Initially, the reaction proceeds by adsorption and activation of H<sub>2</sub> (R1) and CO<sub>2</sub> (R2). Direct dissociation of CO<sub>2</sub> (R3) needs to overcome an activation energy of 0.99 eV and this step is exothermic by 0.81 eV. After CO<sub>2</sub> dissociation, the resulting O\* is removed from the surface as H<sub>2</sub>O *via* two consecutive hydrogenation steps. The H\* located at H<sub>1-6-7</sub> site reacts with O\*, leading to the formation of OH\* (R4, ΔE<sub>act</sub> = 1.40 eV, ΔE<sub>R</sub> = 0.26 eV). After a hydrogen migration step with a minor energy change (ΔE<sub>R</sub> = 0.06 eV), the OH intermediate can be hydrogenated to H<sub>2</sub>O (R5). Including the migration step, this step has activation and reaction energies of 1.39 eV and 1.07 eV, respectively. Finally, the desorption of H<sub>2</sub>O (R6) is endothermic by ΔE<sub>des</sub> = 0.94 eV, leaving an adsorbed CO\* on Ni<sub>8</sub>/TiO<sub>2</sub>-a. This CO\* species can either desorb from the surface (R7) with an energy of 1.93 eV or dissociate to form C\* and O\* (for H-assisted CO\* dissociation, see below). It should be



**Fig. 5** Reaction network for CO<sub>2</sub> hydrogenation on Ni<sub>8</sub>/TiO<sub>2</sub>-a. The numbers correspond to the elementary reaction steps in Tables S1 and S2 and Fig. S8–S11.† The activation energy, adsorption energy, and desorption energy are reported in eV and include a zero-point energy correction (colors: brown: CH<sub>x</sub>-intermediates pathway; red: H<sub>x</sub>CO-intermediates pathway; and orange and blue: H<sub>x</sub>COO-intermediates pathways).





**Fig. 6** The forward and backward activation energies in the network of CO<sub>2</sub> hydrogenation in C<sub>1</sub> chemistry for Ni<sub>8</sub>-TiO<sub>2</sub>-r (colors: brown: CH<sub>x</sub>-intermediates pathway; red: H<sub>x</sub>CO-intermediates pathway; and orange and blue: H<sub>2</sub>COO-intermediates pathways). The energy reported here is zero-energy corrected and given by eV. The cross on COH\*H\* and H<sub>2</sub>COO\* signifies that their formation is impeded by high activation energies, leading to the exclusion of subsequent reactions. The numbers correspond to the elementary reaction steps in Table S1 and S2 and Fig. S12–S15.† The activation energy, adsorption energy, and desorption energy are reported in eV and include a zero-point energy correction.

emphasized that CO desorption can also occur at the states CO\*O\*2H\*, CO\*OH\*H\* and CO\*2H\* with desorption energies of 2.18, 2.16 and 2.17 eV, respectively. These pathways are not explicitly shown in Fig. 5, though they are taken into account in the microkinetic modelling (*vide infra*).

The adsorption of H<sub>2</sub> on the surface containing CO\* (R8) is exothermic by −1.46 eV. The direct dissociation of CO\* (R9, ΔE<sub>act</sub> = 1.99 eV, ΔE<sub>R</sub> = −0.24 eV) generates an adsorbed C\* at F<sub>1–2–7–8</sub> site and an adsorbed O\* at H<sub>5–6–7</sub> site, which can be hydrogenated to CH<sub>4</sub> and H<sub>2</sub>O, respectively. Compared to the direct CO dissociation on Ni<sub>8</sub>/In<sub>2</sub>O<sub>3</sub> (ΔE<sub>act</sub> = 3.24 eV),<sup>62</sup> which shares a similar Ni<sub>8</sub> cluster morphology as Ni<sub>8</sub>/TiO<sub>2</sub> anatase, a lower activation energy is observed on Ni<sub>8</sub>/TiO<sub>2</sub> anatase.

This suggests that Ni/TiO<sub>2</sub> is a more effective catalyst for CO<sub>2</sub> methanation than Ni/In<sub>2</sub>O<sub>3</sub>, the latter mainly producing methanol. In contrast, the work of Sterk *et al.*<sup>65</sup> shows that for the Ni(110) extended surface a relatively low barrier of ΔE<sub>act</sub> = 1.56 eV is found for CO dissociation. Hydrogenation of O\* to OH\* (R10) is endothermic by 0.60 eV with an activation energy of 1.52 eV. The OH\* reacts with another H\* to form an H<sub>2</sub>O molecule (R11, ΔE<sub>act</sub> = 1.46 eV, ΔE<sub>R</sub> = 1.03 eV), which then desorbs from the surface (R12, ΔE<sub>des</sub> = 0.74 eV) and leaves an adsorbed C\* species. H<sub>2</sub> adsorption (R13) provides two H\* with an adsorption energy of −1.60 eV. C\* is subsequently hydrogenated to CH\* (R14, ΔE<sub>act</sub> = 0.88 eV, ΔE<sub>R</sub> = 0.39 eV) and CH<sub>2</sub>\* (R15, ΔE<sub>act</sub> = 0.97 eV, ΔE<sub>R</sub> = 0.70 eV). In





order to form CH<sub>4</sub>, one more H<sub>2</sub> molecule adsorbs (R16,  $\Delta E_{\text{ads}} = -1.86$  eV). The reaction between CH<sub>2</sub>\* and H\* results in the formation of CH<sub>3</sub>\* (R17,  $\Delta E_{\text{act}} = 1.31$  eV,  $\Delta E_{\text{R}} = 0.49$  eV). Next, H\* migrates from B<sub>6-7</sub> to H<sub>1-6-7</sub> resulting in a more stable configuration ( $\Delta E_{\text{R}} = -0.31$  eV). This H\* reacts with CH<sub>3</sub>\* forming CH<sub>4</sub>\* (R18) with an activation energy of 1.41 eV and this step is endothermic by 0.74 eV. The final step is CH<sub>4</sub> desorption (R19) closing the catalytic cycle.

**Pathway involving H<sub>x</sub>CO intermediates.** For many transition metals, it has been observed that when direct C–O bond scission is associated with a prohibitively high barrier, CO dissociation will occur *via* COH\* or HCO\* intermediates.<sup>65</sup> These steps correspond to the red section in Fig. 5. Starting at co-adsorbed CO and H<sub>2</sub> (between R8 and R9), CO\* can become hydrogenated to COH\* (R20) with an activation energy of  $\Delta E_{\text{act}} = 2.27$  eV ( $\Delta E_{\text{R}} = 1.38$  eV). Its subsequent dissociation (R21,  $\Delta E_{\text{act}} = 1.10$  eV,  $\Delta E_{\text{R}} = -1.05$  eV) results in the same configuration of C\*OH\*H\* as found in the direct CO\* dissociation pathway. The overall activation energy for COH\* dissociation is 2.48 eV, which is higher than the activation energy for the direct CO\* dissociation. The alternative pathway proceeds *via* the hydrogenation of CO\* to form HCO\* (R22), which is endothermic by 1.06 eV and has an activation energy of 1.16 eV. Next, the H\* located at H<sub>3-4-8</sub> migrates to a more stable site (B<sub>6-7</sub>) with an exothermic reaction energy of 0.33 eV. HCO\* dissociation generates an adsorbed CH\* and O\* (R23,  $\Delta E_{\text{act}} = 0.93$  eV,  $\Delta E_{\text{R}} = -0.79$  eV). The overall activation energy for the HCO\* formation and dissociation is 1.66 eV, lower than the overall barriers found for direct CO\* dissociation and COH\* pathways, corresponding to 1.99 and 2.48, respectively. The overall activation energy of 1.66 eV lies in between the values found for Ni<sub>8</sub>/In<sub>2</sub>O<sub>3</sub> (1.80 eV)<sup>62</sup> and for a stepped Ni(110)<sup>65</sup> surface (1.21 eV).

After HCO\* dissociation, the O\* reacts with the remaining H\* forming OH\* (R24). The activation energy and reaction energy for OH\* formation are  $\Delta E_{\text{act}} = 1.84$  eV and  $\Delta E_{\text{R}} = 0.67$  eV, respectively, including the migration of H\* and OH\*. H<sub>2</sub> adsorption provides two H\* located at H<sub>1-6-7</sub> and H<sub>3-4-8</sub> (R25,  $\Delta E_{\text{ads}} = -1.28$  eV). The OH\* then is hydrogenated to H<sub>2</sub>O\* (R26,  $\Delta E_{\text{act}} = 1.05$  eV,  $\Delta E_{\text{R}} = 0.81$  eV), which desorbs from the surface (R27) and generates the same configuration of CH\*H\* as found in the direct CO dissociation pathway.

Alternatively, HCO\* can be hydrogenated to form HCOH\* (R29,  $\Delta E_{\text{act}} = 2.28$  eV,  $\Delta E_{\text{R}} = 0.99$  eV), which can alternatively be obtained through COH\* hydrogenation (R28,  $\Delta E_{\text{act}} = 1.25$  eV,  $\Delta E_{\text{R}} = 0.64$  eV). HCOH\* dissociation yields HC\* and OH\* (R30) with an activation energy of 0.95 eV and a reaction energy of -1.43 eV. The overall activation energies of HCOH\* dissociation *via* COH\* and HCO\* are 2.97 eV and 2.98 eV, respectively. Both these pathways are higher in energy than the overall activation energy of HCO\* dissociation, implying that the HCOH\* dissociation pathway is unlikely to occur.

Another mode of H-assisted CO dissociation proceeds *via* the hydrogenation of HCO\* to form H<sub>2</sub>CO\* which can subsequently dissociate (R31 and R32). These two steps require activation energies of 1.19 eV and 2.19 eV, respectively. The corresponding reaction energies are 0.63 eV and -0.60 eV.

The overall activation energy from CO\*2H\* to H<sub>2</sub>C\*O\* is 3.52 eV, implying that this pathway is likely not the most favorable pathway. H<sub>2</sub> adsorption (R33,  $\Delta E_{\text{ads}} = -1.32$  eV) provides two H\* to remove the O\* through the formation of H<sub>2</sub>O. The reaction starts with the interaction of O\* and H\* (R34,  $\Delta E_{\text{act}} = 1.10$  eV,  $\Delta E_{\text{R}} = 0.04$  eV), leading to the formation of OH\* which can be further hydrogenated to H<sub>2</sub>O\* (R35,  $\Delta E_{\text{act}} = 1.99$  eV,  $\Delta E_{\text{R}} = 1.42$  eV). Finally, H<sub>2</sub>O desorbs from the catalyst surface (R36,  $\Delta E_{\text{des}} = 0.70$  eV), leaving behind CH<sub>2</sub>\* as an adsorbate on the catalyst surface and linking back to the CH<sub>x</sub>-intermediates section of the kinetic network.

CH<sub>3</sub>OH formation can proceed *via* twofold hydrogenation of H<sub>2</sub>CO\*. Two H\* are supplied by the adsorption of H<sub>2</sub> (R37,  $\Delta E_{\text{ads}} = -1.23$  eV) after which H<sub>2</sub>CO\* can be hydrogenated to form H<sub>3</sub>CO\* (R40,  $\Delta E_{\text{act}} = 0.91$  eV,  $\Delta E_{\text{R}} = 0.53$  eV). The H<sub>3</sub>CO\* intermediate can be further hydrogenated to form adsorbed CH<sub>3</sub>OH (R47,  $\Delta E_{\text{act}} = 1.80$  eV,  $\Delta E_{\text{R}} = 0.87$  eV) or dissociate into H<sub>3</sub>C\* and O\* (R41,  $\Delta E_{\text{act}} = 0.75$  eV,  $\Delta E_{\text{R}} = -0.25$  eV), the latter being clearly more favorable. The dissociated O\* combines with the H\* forming OH\* (R42) with an activation energy of 0.34 eV. Alternatively, this state can also be obtained *via* H<sub>3</sub>COH\* dissociation (R48,  $\Delta E_{\text{act}} = 0.55$  eV,  $\Delta E_{\text{R}} = -1.70$  eV). H<sub>2</sub> adsorption on the surface containing CH<sub>3</sub>\* and OH\* (R43) is exothermic by 1.34 eV. The resulting H\* atoms can hydrogenate OH\* forming H<sub>2</sub>O (R44,  $\Delta E_{\text{act}} = 1.66$  eV,  $\Delta E_{\text{R}} = 0.38$  eV) which can desorb from the surface with a desorption energy of 1.05 eV (R45) leaving CH<sub>3</sub>\* and H\*.

The last branch in the H<sub>x</sub>CO\* section of the kinetic network involves the conversion of the O-terminated H<sub>2</sub>CO\* intermediate. H<sub>2</sub>CO\* can be hydrogenated to form H<sub>2</sub>COH\* (R38,  $\Delta E_{\text{act}} = 1.58$  eV,  $\Delta E_{\text{R}} = 0.82$  eV) which in turn can dissociate into H<sub>2</sub>C\* and OH\* (R39) with an activation energy of 0.52 eV. This step is exothermic by 1.46 eV. Alternatively, H<sub>2</sub>COH\* is hydrogenated to H<sub>3</sub>COH\* (R46), which is associated with an activation energy of 0.93 eV and an endothermic reaction energy of 0.58 eV.

### 3.2.2.2 Ni<sub>8</sub>/TiO<sub>2-r</sub>

**Pathway involving CH<sub>x</sub> intermediates.** The brown section in Fig. 6 corresponds to the elementary reaction steps among the CH<sub>x</sub> intermediates over Ni<sub>8</sub>/TiO<sub>2-r</sub>. After adsorption of H<sub>2</sub> (R1) and CO<sub>2</sub> (R2), direct dissociation of CO<sub>2</sub>\* generates adsorbed CO\* and O\* (R3,  $\Delta E_{\text{act}} = 0.99$  eV,  $\Delta E_{\text{R}} = -0.21$  eV). The dissociated O\* atom is removed by H\* through the formation and desorption of H<sub>2</sub>O. The formation of OH\* (R4), including a migration of O\* from H<sub>2-7-8</sub> to H<sub>2-3-8</sub>, requires an activation energy of 1.03 eV and is endothermic by 0.25 eV. To facilitate the formation of H<sub>2</sub>O, the remaining H\* needs to migrate to the H<sub>2-3-8</sub> site to be close to the OH\* ( $\Delta E_{\text{R}} = 0.54$  eV). The activation energy and reaction energy for H<sub>2</sub>O\* formation (R5) are 1.25 eV and 0.21 eV, respectively. Finally, the desorption of H<sub>2</sub>O (R6) is endothermic by  $\Delta E_{\text{des}} = 0.74$  eV, leaving an adsorbed CO\* on Ni<sub>8</sub>/TiO<sub>2-r</sub>. This remaining CO\* species can either desorb from the surface (R7) with a desorption energy of  $\Delta E_{\text{des}} = 2.13$  eV or dissociate to form C\* and O\*. Similar to the Ni<sub>8</sub>/TiO<sub>2-a</sub> system, CO desorption can also occur at the states CO\*O\*2H\*,



CO\*OH\*H\* and CO\*2H\* with desorption energies of 2.11, 2.23 and 2.54 eV, respectively. These pathways are not explicitly shown in Fig. 6, though they are taken into account in the microkinetic modelling (*vide infra*).

The adsorption of H<sub>2</sub> on the surface containing CO\* (R8) is exothermic by 1.78 eV. It is important to note that CO can desorb from CO\*2H\*, generating 2H\* species (R66,  $\Delta E_{\text{des}} = 2.54$  eV), which should be considered as a part of the rWGS cycle. A relatively low activation energy of 1.41 eV is required for direct CO\* dissociation (R9,  $\Delta E_{\text{R}} = 0.33$  eV). The dissociated O\* fragment is two-fold hydrogenated to form H<sub>2</sub>O. After the formation of OH\* (R10,  $\Delta E_{\text{act}} = 2.02$  eV,  $\Delta E_{\text{R}} = 0.80$  eV), the OH\* migrates from H<sub>2-7-8</sub> to B<sub>7-8</sub> ( $\Delta E_{\text{R}} = -0.70$  eV). Subsequently the OH\* reacts with the remaining H\* forming H<sub>2</sub>O\* (R11,  $\Delta E_{\text{act}} = 1.42$  eV,  $\Delta E_{\text{R}} = 0.89$  eV). After the desorption of H<sub>2</sub>O (R12,  $\Delta E_{\text{des}} = 0.87$  eV), the C\* undergoes four consecutive hydrogenation steps yielding CH<sub>4</sub>. H<sub>2</sub> adsorption (R13,  $\Delta E_{\text{ads}} = -1.95$  eV) provides two H\* for the hydrogenation of C\* to CH\* (R14,  $\Delta E_{\text{act}} = 1.56$  eV,  $\Delta E_{\text{R}} = 0.71$  eV) and CH<sub>2</sub>\* (R15,  $\Delta E_{\text{act}} = 0.85$  eV,  $\Delta E_{\text{R}} = 0.75$  eV). CH<sub>2</sub>\* will be hydrogenated to CH<sub>3</sub>\* and CH<sub>4</sub>\* by the presence of two H\* (R16,  $\Delta E_{\text{ads}} = -1.84$  eV). CH<sub>3</sub>\* formation (R17) is endothermic by 0.47 eV overcoming an activation energy of 1.34 eV. CH<sub>3</sub>\* migration from T<sub>6-7-8</sub> to B<sub>7-8</sub> ( $\Delta E_{\text{R}} = 0.02$  eV) is followed by the formation of CH<sub>4</sub>. The activation energy and reaction energy for CH<sub>4</sub> formation (R18) are 1.72 eV and 0.86 eV, respectively. Once CH<sub>4</sub> is formed, it desorbs from the catalyst (R19,  $\Delta E_{\text{des}} = 0.15$  eV).

**Pathway involving H<sub>x</sub>CO intermediates.** In the red section of Fig. 6, the elementary reaction steps involving H<sub>x</sub>CO species are shown. Part of this network is comprised of the H-assisted CO dissociation. Due to the high activation energy required to form COH\* formation (R20,  $\Delta E_{\text{act}} = 3.18$  eV), we did not proceed with the calculation of the subsequent COH\* dissociation or COH\* hydrogenation to HCOH\*. The alternative route for CO\* hydrogenation by C-H bond formation leading to HCO\* (R22) has an activation energy of 1.52 eV and is endothermic by 1.17 eV. Subsequent dissociation of HCO\* (R23) results in the formation of CH\* located at H<sub>6-7-8</sub> and O\* located at H<sub>1-4-7</sub>. The activation energy and reaction energy associated with the dissociation of HCO\* are 1.66 eV and -0.60 eV, respectively. Due to the large distance between O\* and H\*, H\* needs to migrate to H<sub>1-2-7</sub> site first ( $\Delta E_{\text{R}} = 0.35$  eV). Formation of OH\* (R24) requires an activation energy of 1.21 eV, accompanied by a reaction energy of 0.20 eV. H<sub>2</sub> adsorption (R25) provides H\* to hydrogenate the OH\* to H<sub>2</sub>O\* and is associated with an adsorption energy of -1.41 eV. OH\* reacts with H\* located at H<sub>2-7-8</sub> forming H<sub>2</sub>O (R26,  $\Delta E_{\text{act}} = 1.81$  eV,  $\Delta E_{\text{R}} = 0.91$  eV), which desorbs generating CH\*H\* (R27,  $\Delta E_{\text{des}} = 0.32$  eV), linking back to the CH<sub>x</sub>-intermediates section. HCO\* can be hydrogenated to HCOH\* (R29) by overcoming an activation energy of 2.04 eV. The formation of HCOH\* is endothermic by 1.46 eV. HCOH\* can be dissociated into CH\* and OH\* (R30) with an activation energy of  $\Delta E_{\text{act}} = 0.19$  eV and a reaction energy of  $\Delta E_{\text{R}} = -1.51$  eV.

HCO\* can undergo hydrogenation to form H<sub>2</sub>CO\* (R31,  $\Delta E_{\text{act}} = 1.25$  eV,  $\Delta E_{\text{R}} = 0.61$  eV), which then dissociates into H<sub>2</sub>C\* and O\* by overcoming an activation energy barrier of 1.41 eV (R32). The dissociation of H<sub>2</sub>CO\* is exothermic by 0.89 eV. The O\* species is subsequently hydrogenated to H<sub>2</sub>O\*. The adsorption of H<sub>2</sub> on the surface containing H<sub>2</sub>C\* and O\* is exothermic by 1.10 eV (R33). The initial hydrogenation of O\* leads to the formation of OH\* (R34), involving an activation energy of 1.30 eV and a reaction energy of 0.40 eV. The migration of H\* occurs to react with OH\* and form H<sub>2</sub>O ( $\Delta E_{\text{R}} = 0.52$  eV). Subsequently, the formation of H<sub>2</sub>O (R35) is endothermic by 0.65 eV, requiring an activation energy of 1.65 eV. Finally, H<sub>2</sub>O desorbs into the gas phase (R36) with a reaction energy of 0.33 eV and leaving an adsorbed CH<sub>2</sub>\* species on the surface. The subsequent hydrogenation of CH<sub>2</sub>\* to CH<sub>4</sub> has been discussed in the CH<sub>x</sub>\* intermediates pathway (*vide supra*).

The adsorption of H<sub>2</sub> on the surface containing H<sub>2</sub>CO\* provides two H\* species, which are subsequently utilized for the hydrogenation of H<sub>2</sub>CO\*. This adsorption process is exothermic by 1.56 eV (R37). Hydrogenation of H<sub>2</sub>CO\* can occur either *via* hydrogenation at the O-terminus or at the C-terminus, resulting in the formation of H<sub>2</sub>COH\* (R38,  $\Delta E_{\text{act}} = 1.52$  eV,  $\Delta E_{\text{R}} = 1.27$  eV) or H<sub>3</sub>CO\* (R40,  $\Delta E_{\text{act}} = 0.92$  eV,  $\Delta E_{\text{R}} = 0.53$  eV), respectively. The dissociation of H<sub>2</sub>COH\* gives rise to H<sub>2</sub>C\*OH\*H\* (R39,  $\Delta E_{\text{act}} = 0.46$  eV,  $\Delta E_{\text{R}} = -1.29$  eV), which serves as an intermediate in the H<sub>2</sub>CO\* dissociation pathway. H<sub>3</sub>CO\* resulting from H<sub>2</sub>CO\* hydrogenation can either undergo another hydrogenation step to form H<sub>3</sub>COH\* (R47) or dissociate into H<sub>3</sub>C\* and O\* (R41). The dissociation of H<sub>3</sub>CO\* is more favorable, exhibiting an activation energy of  $\Delta E_{\text{act}} = 0.88$  eV and is exothermic by  $\Delta E_{\text{R}} = -1.17$  eV. In comparison, its hydrogenation has an activation energy of  $\Delta E_{\text{act}} = 2.23$  eV and a reaction energy of  $\Delta E_{\text{R}} = 1.18$  eV. Upon the dissociation of H<sub>3</sub>CO\*, the O\* reacts with the remaining H\* forming OH\* (R42,  $\Delta E_{\text{act}} = 1.71$  eV,  $\Delta E_{\text{R}} = 0.52$  eV). This configuration can alternatively be obtained through the dissociation of the C-O bond in H<sub>3</sub>COH\* (R48,  $\Delta E_{\text{act}} = 0.83$  eV,  $\Delta E_{\text{R}} = -1.83$  eV). The OH\* is hydrogenated to H<sub>2</sub>O\* in the presence of H\* (R44,  $\Delta E_{\text{act}} = 1.92$  eV,  $\Delta E_{\text{R}} = 1.21$  eV). The H\* is provided by the adsorption of H<sub>2</sub> (R43), which is exothermic by 1.17 eV. Finally, H<sub>2</sub>O desorbs from the surface with a desorption energy of 0.19 eV (R45). On the surface, there exist a CH<sub>3</sub>\* species along with a remaining H\* species, and the reaction between these two entities has been previously described within the context of the CH<sub>x</sub>\* intermediates pathway. Finally, hydrogenation of H<sub>2</sub>COH\* leads to the formation of H<sub>3</sub>COH\* with an activation energy of 0.97 eV and a reaction energy of 0.44 eV (R46), which can desorb from the surface (R49,  $\Delta E_{\text{des}} = 0.68$  eV).

**3.2.2.3 Comparison of reaction networks.** Overall, our investigations on both Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r surfaces indicate that the direct dissociation of CO<sub>2</sub> is favored over H-assisted CO<sub>2</sub> dissociation. The corresponding reaction energy diagrams for this pathway is shown in Fig. S16.† This finding aligns with the observations made by Zhang *et al.*,



who conducted DFT calculations on Ni<sub>4</sub>/CeO<sub>2</sub> (111) and reported activation energies of 2.55 eV for HCOO\* formation, 2.80 eV for COOH\* formation, and 1.60 eV for CO<sub>2</sub> direct dissociation.<sup>66</sup>

The activation energy for the direct dissociation of CO\* on Ni<sub>8</sub>/TiO<sub>2</sub>-a is 1.88 eV. In comparison, the overall activation energy for HCO\* formation and dissociation is 1.66 eV whereas the overall activation energy for H<sub>2</sub>CO\* formation *via* CO\*2H\* → HCO\*H\* → H<sub>2</sub>CO\* is 1.92 eV. Based on these values, the H-assisted CO\* dissociation *via* HCO\* is energetically the most favorable pathway. For Ni<sub>8</sub>/TiO<sub>2</sub>-r, it was found that direct dissociation of CO\* requires an activation energy of 1.41 eV. In comparison, the overall activation energy for HCO\* formation and dissociation is 2.83 eV while the overall activation energy for H<sub>2</sub>CO\* formation is 2.42 eV. Based on these numbers, direct CO\* dissociation is energetically the most likely pathway over Ni<sub>8</sub>/TiO<sub>2</sub>-r.

Finally, comparing Ni<sub>8</sub>/TiO<sub>2</sub>-r to Ni<sub>8</sub>/TiO<sub>2</sub>-a, the former exhibits a lower activation energy for the direct dissociation of CO\*, but the subsequent hydrogenation steps are associated with higher barriers. For example, the overall activation energy for CH<sub>3</sub>\* hydrogenation to CH<sub>4</sub> on Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r are 1.59 eV and 2.18 eV, respectively. Nevertheless, assessment of the most facile pathways purely based on the DFT energetics remains in absence of the surface coverages limited and microkinetics simulations are conducted to further study the kinetic behavior of these systems.

### 3.3 Microkinetics simulations

Microkinetics simulations are conducted to predict the catalytic performance of Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r for CO<sub>2</sub> hydrogenation. The activation energies and pre-exponential factors as determined by DFT were employed for these microkinetics simulations.

Fig. 7 depicts the reaction rate and product distribution for Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r. Ni<sub>8</sub>/TiO<sub>2</sub>-a exhibits a significantly higher CO<sub>2</sub> conversion rate than Ni<sub>8</sub>/TiO<sub>2</sub>-r. These turn-over-frequencies are lower than those observed by Liu *et al.*, who

report a TOF = 2.14 × 10<sup>-3</sup> for Ni nanoparticles of 2.2 nm at a temperature of T = 200 °C.<sup>67</sup> Abir *et al.* reported a TOF = 2 × 10<sup>-2</sup> for 2.9 nm particles at T = 350 °C.<sup>68</sup> In both studies, a mixed anatase/rutile support was used. In contrast, Li *et al.* report a TOF = 5.1 × 10<sup>1</sup> s<sup>-1</sup> for 1 nm particles supported on TiO<sub>2</sub>-anatase at T = 500 °C.<sup>69</sup> These latter results align well to our results found for Ni<sub>8</sub>/TiO<sub>2</sub>-a. At low temperature, both surface models produce mainly CH<sub>4</sub>, while the selectivity to CO increases with temperature at the expense of the CH<sub>4</sub> selectivity. The selectivity towards CH<sub>3</sub>OH is negligible at all temperatures considered. At a temperature of 350 K, Ni<sub>8</sub>/TiO<sub>2</sub>-a only produces CH<sub>4</sub>, while the CH<sub>4</sub> selectivity for Ni<sub>8</sub>/TiO<sub>2</sub>-r is 85%.

To determine the dominant pathway for CO<sub>2</sub> hydrogenation within the chemokinetic network of Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r, a reaction pathway analysis is conducted. Fig. S17 and S18† provide the molar rate fluxes for Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r at T = 600 K. The dominant reaction pathways for product formation at this temperature are indicated in Fig. 8. For both models, direct dissociation of CO<sub>2</sub> is preferred over H-assisted CO<sub>2</sub> dissociation. The manner of CO dissociation differs between Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r. On Ni<sub>8</sub>/TiO<sub>2</sub>-a, the former favors H-assisted CO dissociation while the latter favors direct CO\* dissociation.

To determine which steps control the overall activity and selectivity, DRC and DSC analyses (with respect to CO<sub>2</sub> consumption) are conducted. Fig. 9a shows that at low temperature, the desorption of H<sub>2</sub>O (R6 in Fig. 5) is the rate-determining step on Ni<sub>8</sub>/TiO<sub>2</sub>-a. The dominant species on the surface is CO\*O\*2H\* (Fig. 9b). This observation can be attributed to the fact that the elementary reactions R4, R5, and R6 in Fig. 5 are endothermic. As such, CO\*O\*2H\* is the state lowest in energy prior to the rate-determining step R6 which consequently becomes the most abundant state under these conditions. From Fig. 9c, we can see that the apparent activation energy is around 200 kJ mol<sup>-1</sup> at low temperature and decreases with increasing temperature. This result can be rationalized from Fig. 9g which shows the potential energy diagram for CH<sub>4</sub> formation *via* the HCO\* dissociation pathway. The dominant intermediary state is highlighted in

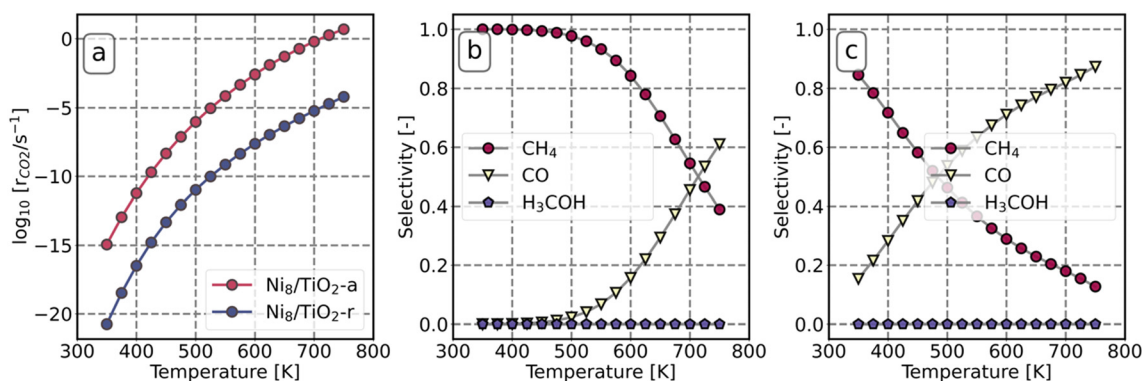
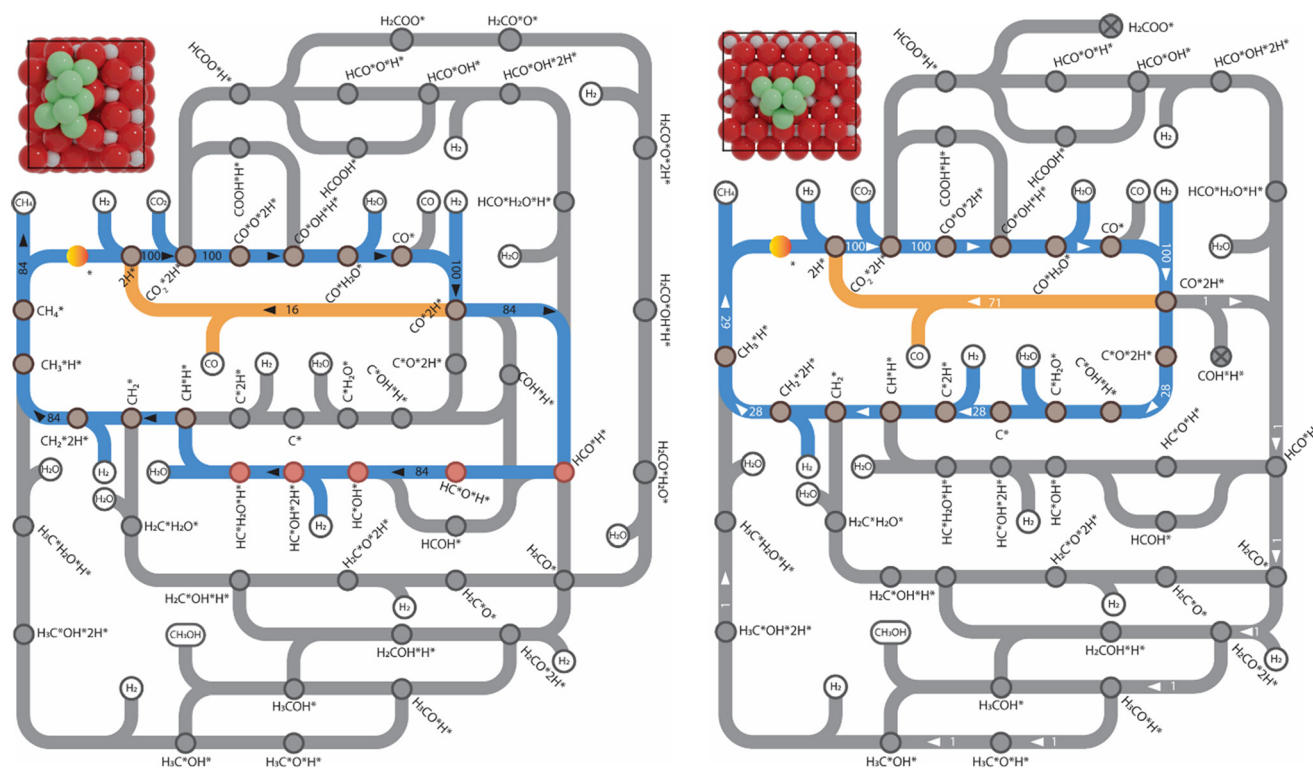


Fig. 7 Reaction rate of CO<sub>2</sub> as a function of temperature (a). The selectivity of CO, CH<sub>4</sub> and H<sub>3</sub>COH as a function of temperature on Ni<sub>8</sub>/TiO<sub>2</sub>-a (b) and Ni<sub>8</sub>/TiO<sub>2</sub>-r (c).







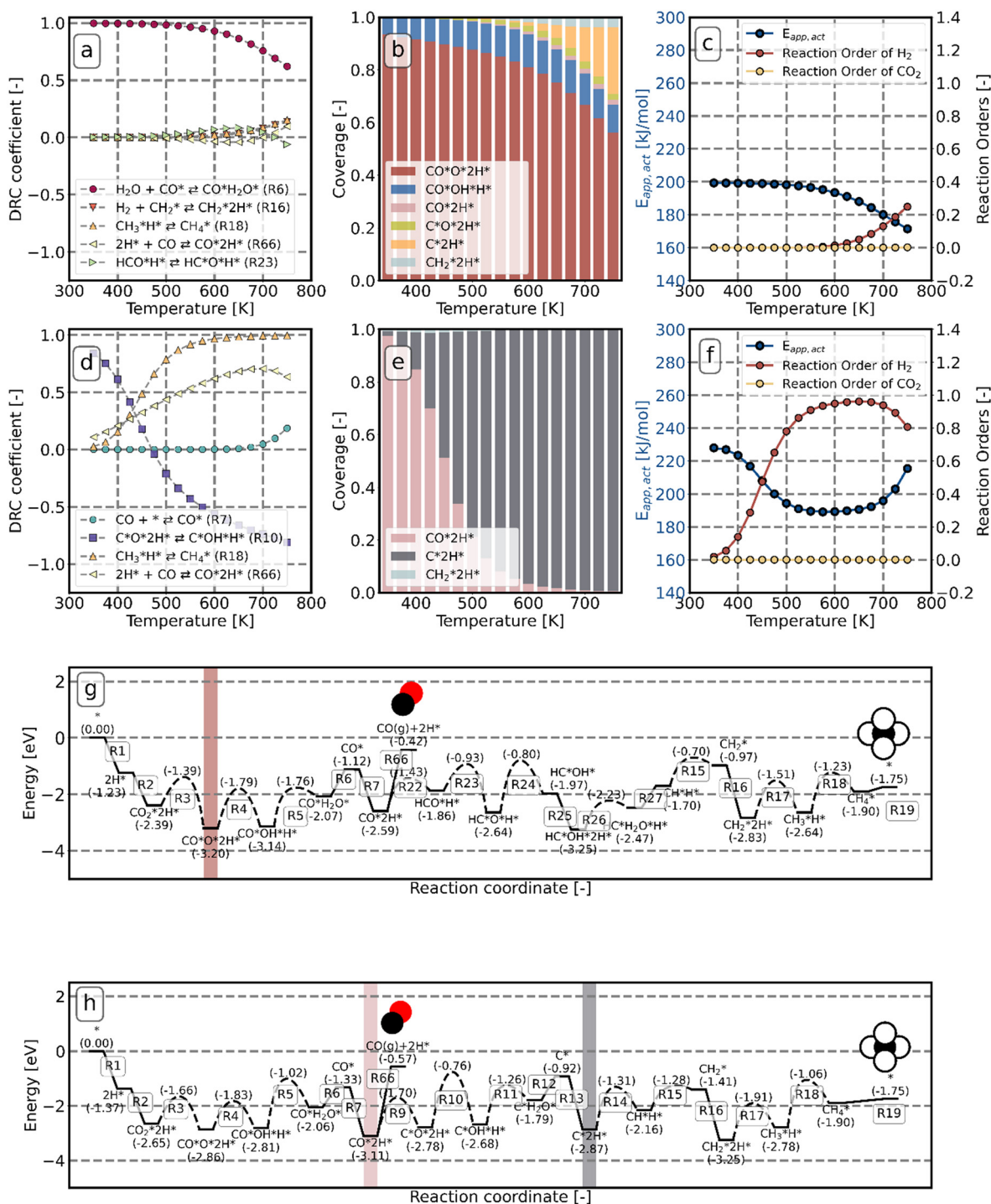
**Fig. 8** Preferred pathways for CO<sub>2</sub> hydrogenation on Ni<sub>8</sub>/TiO<sub>2</sub>-a (left) and Ni<sub>8</sub>/TiO<sub>2</sub>-r (right). The production of CO and CH<sub>4</sub> is represented by the yellow and blue paths, respectively. All values are normalized with respect to the rate of adsorbed CO<sub>2</sub> and are given in percentages (%).

red and the overall barrier for H<sub>2</sub>O desorption (the rate-determining step) with respect to this state is determined to be 2.08 eV, which is in agreement with the apparent activation energy. The reaction orders are in line with this observation. Since the dominant CO\*O\*2H\* state already has two hydrogen atoms present, no further hydrogen is necessary to proceed towards the rate-determining step and consequently the reaction order in H<sub>2</sub> (Fig. 9c) is observed to be zero. Likewise, since the dominant state already represents the fragments of CO<sub>2</sub> dissociation, a reaction order of 0 in CO<sub>2</sub> is found.

At temperatures between  $T = 500$  K and  $T = 650$  K, H<sub>2</sub>O desorption becomes less rate-limiting to the rate of CO<sub>2</sub> consumption while HCO\*H\*  $\rightleftharpoons$  HC\*O\*H\* (R23) and CH<sub>3</sub>\* hydrogenation (R18) becomes more rate-limiting. Simultaneously, it is observed that CO desorption (R66) becomes rate-inhibiting. Due to the increase in temperature, there is more thermal energy available to overcome the H<sub>2</sub>O desorption barrier resulting in barriers further down the kinetic pathway to become rate-limiting. Since CO desorption (R66) prevents the formation of CH<sub>4</sub> which is still the dominant product under these conditions, this step is rate-inhibiting. Further increasing the temperature above  $T = 650$  K results in further decreasing the degree of rate control of the H<sub>2</sub>O desorption reaction. Simultaneously, HCO\*H\*  $\rightleftharpoons$  HC\*O\*H\* (R23) becomes rate-inhibiting, whereas CH<sub>3</sub>\* hydrogenation (R18) and CO desorption (R66) become rate-limiting. These changes reflect the change in selectivity from

CH<sub>4</sub> to CO. At elevated temperature, the dominant pathway switches from CH<sub>4</sub> production *via* the HCO\* intermediate to a rWGS pathway *via* R66. Since H<sub>2</sub>O desorption is a step in the kinetic network for both CO as well as CH<sub>4</sub> production, this step remains rate-limiting to some extent. CH<sub>3</sub>\* hydrogenation is also still a rate-limiting step as even at elevated temperature there remains a significant selectivity towards CH<sub>4</sub>. Nevertheless, the rate of CO<sub>2</sub> consumption for CH<sub>4</sub> production is lower than for CO and a change in selectivity towards CH<sub>4</sub> by lowering the barrier for HCO\*H\*  $\rightleftharpoons$  HC\*O\*H\* would result in a decreased overall activity, explaining why this step becomes rate-inhibiting at elevated temperature. The DSC analysis as shown in Fig. S19† further reflects upon this. From this figure, it can be seen that HCO\*H\*  $\rightleftharpoons$  HC\*O\*H\* and CO\* desorption control the selectivity between CH<sub>4</sub> and CO. The apparent activation energy and reaction orders change accordingly as a function of temperature. With increasing temperature, the catalyst tends to reside in states further down the kinetic pathway with respect to CO\*O\*2H\*, specifically CO\*OH\*H\*, CO\*2H\*, C\*O\*2H\*, C\*2H\* and CH<sub>3</sub>\*2H\*. From Fig. 9f it can be readily seen that these states are all higher in energy with respect to CO\*O\*2H\*. With respect to the barrier of the dominant rate-limiting step for these intermediates, *i.e.* either CH<sub>3</sub>\* hydrogenation or CO\* desorption, the energy difference is somewhat smaller than between CO\*O\*2H\* and the barrier for H<sub>2</sub>O\* desorption. Since all these intermediary species already contain fragments arising from CO<sub>2</sub>\* adsorption, the





**Fig. 9** Degree of rate-control coefficient with respect to CO<sub>2</sub> consumption (a and d), the steady state of surface coverage (b and e), the apparent activation (c and f), the reaction orders of CO<sub>2</sub> and H<sub>2</sub> (c and f) as a function of temperature. Ni<sub>8</sub>/TiO<sub>2</sub>-a: a–c; Ni<sub>8</sub>/TiO<sub>2</sub>-r: d–f. The potential energy diagram of CO<sub>2</sub> methanation on Ni<sub>8</sub>/TiO<sub>2</sub>-a (g) and Ni<sub>8</sub>/TiO<sub>2</sub>-r (h). In figures (g) and (h), the predominant species are accentuated using consistent color coding in the coverage plots.

reaction order in CO<sub>2</sub> remains zero. In contrast, with the exception of CH<sub>2</sub>\*2H\*, all other abundant intermediary states require the adsorption of another H<sub>2</sub> molecule in order to proceed to the rate-limiting step of CH<sub>3</sub>\* hydrogenation. Consequently, the increased reaction order in H<sub>2</sub> reflects the decrease in surface abundance of CO\*O\*2H\* in favor of a

number of intermediates that are precursor species towards CH<sub>4</sub> formation that requires the adsorption of H<sub>2</sub> to produce CH<sub>4</sub>.

In Fig. 9d, the DRC analysis for Ni<sub>8</sub>/TiO<sub>2</sub>-r is shown. At low temperatures, the reaction is mainly controlled by the rate of C\*O\*2H\* ⇌ C\*OH\*H\* (R10) and CO\*2H\* is the most



abundant cluster configuration. The desorption of CO requires 2.54 eV, whereas the activation energy between CO\*2H\* and R10 is 2.35 eV. At low temperature CH<sub>4</sub> formation is preferred, yet the selectivity towards CH<sub>4</sub> rapidly decreases in favor of CO with increasing temperature as desorption rates increase more rapidly with increasing temperature in comparison to surface reactions. With increasing temperature, the degree of rate-control of step R10 decreases in favor of CO\* desorption (R66) and CH<sub>3</sub> hydrogenation (R18) becoming rate-limiting steps. A further increase in temperature results in C\*O\*2H\*  $\rightleftharpoons$  C\*OH\*H\* becoming rate-inhibiting while the degree of rate-control for CO\* desorption and CH<sub>3</sub> hydrogenation increase further. From Fig. 9e, it is found that CO\*2H is the dominant surface state at the low temperature regime whereas with increase in temperature C\*2H\* becomes the most abundant surface state. The change in surface coverage reflects the degree of rate control for C\*O\*2H\*  $\rightleftharpoons$  C\*OH\*H\*. When this step is rate-controlling, the state lowest in energy prior to the barrier of this step corresponds to CO\*2H\*. When this step is no longer rate-limiting due to the increase in temperature, the state C\*2H\* is the next state lowest in energy prior to one of the rate-limiting steps (*i.e.* R18 and R66).

The apparent activation energy and the reaction orders as shown in Fig. 9f are in line with these trends. At low temperature, a value of 230 kJ mol<sup>-1</sup> is found, corresponding to the difference in energy between the CO\*2H state (Fig. 9h, highlighted in pink) and the height of the transition state for C\*O\*2H hydrogenation. With increasing temperature, the system spends more time in the C\*2H\* state which lies higher in energy. Consequently, the apparent activation energy decreases. In contrast to the low temperature situation, a facile quantitative comparison between the energy levels of the states in the potential energy diagram and the apparent activation energy is not possible for the high temperature situation as no single elementary reaction step is predominantly rate-controlling. The increase in the apparent activation energy for  $T > 700$  K is caused by the deposition of carbonaceous species leading to catalyst deactivation. The observation that C\*O\*2H\* hydrogenation is strongly rate-inhibiting is in line with this observation. As this step becomes more facile, O\* that could otherwise be used to recombine with C\* to form CO\* which can desorb from the surface, is now removed as H<sub>2</sub>O. In absence of O\* and with C\* + 2H\* being very stable on the surface, further progression towards CH<sub>4</sub> is prevented. The branch in the kinetic network *via* R9–R13 effectively leads to a dead state of the catalyst. Finally, Fig. 9f shows that the reaction order in CO<sub>2</sub> remains close to zero, irrespective of temperature whereas the reaction order in H<sub>2</sub> increases as a function of temperature. Since both the CO\*2H\* intermediate and the C\*2H\* intermediates already contain the dissociation fragments of CO<sub>2</sub> necessary for the rate-limiting steps to proceed, an increase or decrease in the partial pressure of CO<sub>2</sub> will not affect the overall rate. In contrast, in the high temperature regime the dominant state lacks 2H\* species for

the CH<sub>3</sub>\* + H\* reaction to proceed. The reaction order in H<sub>2</sub> therefore reflects the extent to which this pathway controls the overall reaction rate. At temperatures  $T > 700$  K, we however observe that the reaction order in H<sub>2</sub> slightly decreases. Here, additional H\* is detrimental to the activity of the catalyst as it leads to further O\* removal and thus the formation of strongly bound C\*.

Conclusively, the lower reactivity observed for the Ni<sub>8</sub>/TiO<sub>2</sub>-r system in comparison to Ni<sub>8</sub>/TiO<sub>2</sub>-a is caused by the presence of a relative facile direct CO dissociation. The low barrier for CO dissociation coincides with C\* being strongly bound to the catalyst leading to catalyst deactivation. In contrast, for Ni<sub>8</sub>/TiO<sub>2</sub>-a, direct CO dissociation is difficult, and a H-assisted pathway is more facile. This is already indicative for C\* being less strongly bound to the catalyst benefiting its activity. These results are according to the Sabatier principle which shows that although strong adsorption leads to facile activation of the adsorbates, it prevents the desorption of the products, poisoning the catalyst.

As the utilization of the PBE functional commonly leads to an overestimation of the binding energy of CO,<sup>70–72</sup> we need to critically assess its effect. As such, additional microkinetic simulations were conducted wherein simultaneously the CO and CO<sub>2</sub> adsorption energy were decreased in a range of 0.0 to 0.3 eV on both Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r models, ensuring that this modification does not affect the overall thermodynamics of the reaction. The resulting reaction rates of CO<sub>2</sub> and selectivity were analyzed and summarized in Fig. S26 and S27.† Decreasing the CO adsorption energy on both Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r catalysts results in an increase in the CO selectivity. For these two surfaces, CO becomes the main product when the correction of CO adsorption energy was set to 0.3 eV at 600 K.

Although we established that H-spillover is associated with relatively high barriers, we nevertheless explored the effect of an enhanced H\* coverage on the Ni<sub>8</sub>-clusters. This analysis was however limited to CO and HCO dissociation and HCO formation as these steps were found to affect the selectivity of the reaction (Fig. S19)†. As we determined H-spillover to be difficult, thus assuming that accumulation of additional H\* species on the clusters would proceed *via* adsorption from the gas phase, we furthermore calculated the adsorption energy of H<sub>2</sub> as function of the H\* coverage. The results are shown in Tables S3–S5 in the ESI.† From Tables S3 and S4,† it can be seen that on Ni<sub>8</sub>/TiO<sub>2</sub>-anatase, the overall activation energies for HCO\* formation and dissociation are always higher than the activation energies for direct dissociation of CO\*. Conversely, on the Ni<sub>8</sub>/TiO<sub>2</sub> rutile surface, the direct CO\* dissociation exhibits a lower activation energy as compared to the HCO\* formation and dissociation. Therefore, the conclusion that Ni<sub>8</sub>/TiO<sub>2</sub> anatase predominantly follows the HCO\* pathway while Ni<sub>8</sub>/TiO<sub>2</sub>-rutile favors the direct CO\* dissociation pathway remains valid, irrespective of the H\* coverage. Furthermore, from Table S5† it can be observed that additional H\* accumulation is associated with a significantly decreased





adsorption energy. Given the loss of entropy of H<sub>2</sub> upon adsorption, we estimate, especially at higher temperature, that the presence of more than two H\* species, in addition to H<sub>x</sub>CO, on the Ni<sub>8</sub> clusters is highly unlikely.

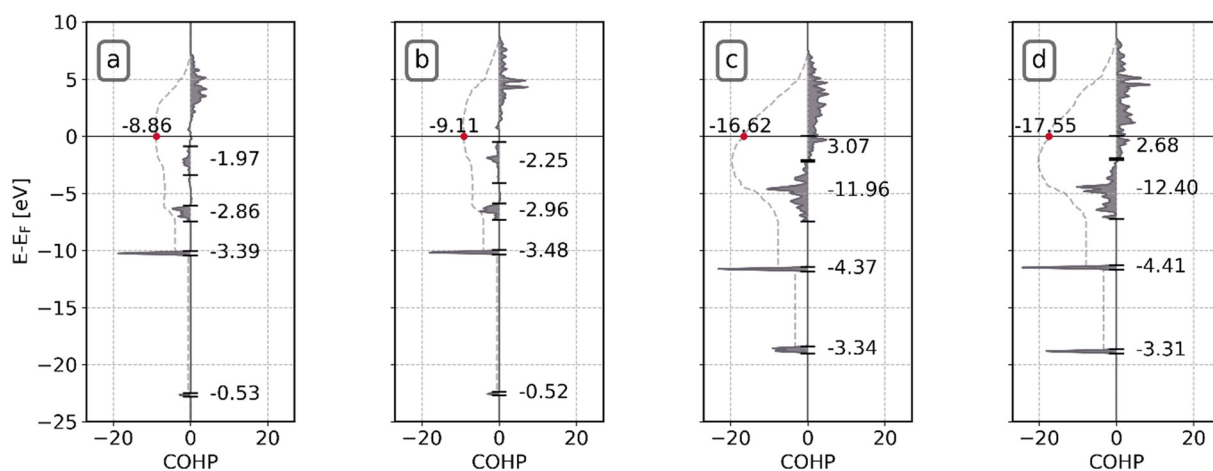
From these additional simulations we can conclude that the Ni<sub>8</sub> clusters have a vastly lower activity as compared to experiment,<sup>67,68</sup> even when taking potential effects of overbinding and H-accumulation into account. Despite that Ni<sub>8</sub>/TiO<sub>2</sub>-r allows for a direct CO dissociation, it results in the formation of a very stable C\* species effectively poisoning the catalyst surface. This poisoning condition is less severe on Ni<sub>8</sub>/TiO<sub>2</sub>-a, yet compared to extended Ni surfaces, also here much higher adsorption energies are observed for the reaction intermediates. We assign the increased adsorption strength of CO\* and C\* to the presence of coordinatively undersaturated Ni atoms in these clusters, which due to the specific alignment of the Ni atoms with the support, lead to much stronger adsorption energies for Ni<sub>8</sub>/TiO<sub>2</sub>-rutile as compared to Ni<sub>8</sub>/TiO<sub>2</sub>-anatase.

### 3.4 Electronic structure analysis

Microkinetic simulations show that for both Ni<sub>8</sub>/TiO<sub>2</sub>-a as well as Ni<sub>8</sub>/TiO<sub>2</sub>-r the initial C–O bond scission in CO<sub>2</sub> proceeds in a direct fashion. After removal of the dissociated O\* fragment as H<sub>2</sub>O, the remaining CO\* fragment needs to dissociate as well for CH<sub>4</sub> formation. For this step, the two models differ in the preferred pathway as shown in Fig. 8. For Ni<sub>8</sub>/TiO<sub>2</sub>-a, C–O bond scission proceeds in a H-assisted fashion *via* an HCO\* intermediate, whereas for Ni<sub>8</sub>/TiO<sub>2</sub>-r it proceeds in a direct fashion. This observation can be readily explained based on the activation energies. The activation energy of CO direct dissociation for Ni<sub>8</sub>/TiO<sub>2</sub>-r is 1.41 eV, whereas for Ni<sub>8</sub>/TiO<sub>2</sub>-a a higher activation energy of 1.99 eV is found. The barriers for CO\* hydrogenation to HCO\* and its subsequent dissociation to CH\* and O\* are 1.16 eV and 0.93

eV. Despite the initial hydrogenation step being endothermic by 0.70 eV, the effective barrier for the H-assisted step is 1.66 eV, making the H-assisted pathway preferred over the direct pathway.

To better understand the differences in the activation energies of CO\* direct dissociation, we performed a density of states (DOS) and Crystal Orbital Hamilton Population (COHP) analysis on CO\* and the transition state of its dissociation towards C\* + O\* for Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r. The results of this analysis are shown in Fig. 10 and S24.† In Fig. S21a and f,† the DOS and COHP for the C–O interaction of CO in the gas phase is shown. Note that a more negative COHP coefficient indicates that the Kohn–Sham states provide a bonding contribution to the pair of atoms, while a more positive COHP coefficient indicates that the Kohn–Sham state provides a more anti-bonding contribution. Fig. S21a† displays the canonical molecular orbitals of CO and their occupancies. These molecular orbitals are commonly divided among  $\sigma$ - and  $\pi$ -type orbitals based on the presence or absence of a nodal plane alongside the C–O bonding axis. It can be readily observed that the number of valence electrons of CO in the gas phase corresponds to 10. From Fig. S21f,† the bonding character for each of the orbitals is seen including the integrated COHP (iCOHP) at the Fermi level which is a quantitative measure of the C–O bond strength. Upon adsorption, we can see from Fig. S24a and c† that the 3 $\sigma$  and 4 $\sigma$  interactions are largely unchanged due to a limited mixing of these molecular orbitals with the d-orbitals on Ni. In contrast, the 1 $\pi$  and 5 $\sigma$  orbitals show pronounced mixing as evidenced by the broadening of the peaks. Furthermore, due to the mixing of the anti-bonding 2 $\pi^*$  orbitals with the d-orbitals on Ni, the newly formed states derived from these orbitals descent below the Fermi level and become occupied. The integrated DOS (iDOS) at the Fermi level for adsorbed CO shows that the electron density around CO increases, in line with the higher electronegativity



**Fig. 10** COHP analysis of Ni–CO bonds in the initial state (IS) and transition state (TS) of CO direct dissociation on Ni<sub>8</sub>/TiO<sub>2</sub>-a and Ni<sub>8</sub>/TiO<sub>2</sub>-r. (a) IS on Ni<sub>8</sub>/TiO<sub>2</sub>-a; (b) IS on Ni<sub>8</sub>/TiO<sub>2</sub>-r; (c) TS on Ni<sub>8</sub>/TiO<sub>2</sub>-a; (d) TS on Ni<sub>8</sub>/TiO<sub>2</sub>-r. The numeric values above Fermi level indicate the integrated COHP (iCOHP).



of CO as compared to Ni and resulting in the occupation of the anti-bonding orbitals. The occupation of these anti-bonding orbitals together with the reduction in bonding character of the  $1\pi$ -type orbitals lead to an activation of the CO molecule, as evidenced by the reduced iCOHP value shown in Fig. S21† corresponding to  $-15.86$  and  $-16.09$  for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  and  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , respectively. These values are however sufficiently similar that we cannot attribute the difference in the dissociation barrier to a difference in the activation of the CO molecule upon adsorption. The C–O interaction in the transition state, as shown in Fig. S21,† are also substantially similar from which we infer that both clusters have the same propensity towards activating CO and we hypothesize that the difference in the CO dissociation barrier should therefore be caused by differences in the stabilization of the pre-dissociated fragments in the transition state. It should be noted that this result contrasts with CO activation patterns typically found for extended metals, as showcased in the work of Fariduddin *et al.*<sup>73</sup>

To test our hypothesis, in Fig. 10a–d, a COHP analysis is conducted for the Ni–CO interaction. Similar to the results found for the C–O interaction, here the COHP acts as a metric to assess the interaction strength between the cluster and the  $\text{C}^*$  and  $\text{O}^*$  fragments. The iCOHP values for adsorbed  $\text{CO}^*$ , *i.e.* in the initial state, at the Fermi level are  $-8.86$  and  $-9.11$  for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  and  $\text{Ni}_8/\text{TiO}_2\text{-r}$ . These values are in line with the observed adsorption heats of  $-2.14$  eV and  $-2.54$  eV for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  and  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , respectively. For the transition state, significantly lower iCOHP values of  $-16.62$  and  $-17.55$  are found for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  and  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , respectively. Clearly,  $\text{Ni}_8/\text{TiO}_2\text{-r}$  shows a significant increase in the Ni–CO interaction strength between the TS and IS in comparison to  $\text{Ni}_8/\text{TiO}_2\text{-a}$ , explaining the much lower reaction barrier observed. We attribute this enhanced bonding interaction of pre-dissociated  $\text{C}^*$  and  $\text{O}^*$  in the transition state on  $\text{Ni}_8/\text{TiO}_2\text{-r}$  to the presence of a very stable fivefold adsorption site for C, whereas for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  a less favorable quasi-fourfold adsorption site is present (as shown in Fig. S25†). This five-fold site of  $\text{Ni}_8/\text{TiO}_2\text{-r}$  hosts a square-planar motif for which exceptional stability for  $\text{C}^*$  has been identified earlier in the work of Nandula *et al.*<sup>74</sup>

Conclusively, a critical factor in the preferred kinetic pathway is assigned to the presence of a low CO dissociation barrier. In the absence of such a barrier, a H-assisted route is preferred as seen for  $\text{Ni}_8/\text{TiO}_2\text{-a}$ . In contrast,  $\text{Ni}_8/\text{TiO}_2\text{-r}$  allows for a direct CO dissociation due to the availability of an active motif for which the COHP analysis predicts enhanced stability for the dissociation fragments.

## 4. Conclusions

In this study, the effect of the  $\text{TiO}_2$  phase, anatase or rutile, on  $\text{CO}_2$  hydrogenation over small  $\text{Ni}_8$  cluster was investigated. Using a hybrid genetic algorithm/density functional theory approach, the putative global minimum structure for  $\text{Ni}_8$  clusters supported on the most stable anatase and rutile surface

terminations were searched. Due to different metal–support interactions, the  $\text{Ni}_8$  clusters adopt different morphologies on anatase and rutile  $\text{TiO}_2$ .

By means of density functional theory calculations, all elementary reaction steps relevant to  $\text{CO}_2$  hydrogenation, *i.e.* direct and H-assisted  $\text{CO}_2$  and CO dissociation as well as subsequent hydrogenation steps to form  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  were calculated. By means of microkinetic modelling, we observed that the anatase supported  $\text{Ni}_8$  clusters yielded a higher activity towards  $\text{CO}_2$  consumption as compared to the rutile equivalent. For both clusters, at the low temperature the selectivity is mainly towards  $\text{CH}_4$  whereas with increasing temperature, the selectivity switches to CO. The amount of  $\text{CH}_3\text{OH}$  produced remains negligible.

Both catalysts exhibit direct  $\text{CO}_2$  dissociation.  $\text{Ni}_8/\text{TiO}_2\text{-r}$  shows direct dissociation whereas for  $\text{Ni}_8/\text{TiO}_2\text{-a}$  the H-assisted route *via* a  $\text{HCO}^*$  intermediate is preferred. Analysis of the reaction energy diagram and the DFT calculations reveal that this difference can be assigned to the stronger adsorption for carbonaceous species on  $\text{Ni}_8/\text{TiO}_2\text{-r}$  as compared to  $\text{Ni}_8\text{-TiO}_2\text{-a}$ . Not only leads this to a lower barrier for direct dissociation for the former catalyst, it also leads to the reaction intermediates being too strongly bound to the catalyst, effectively deactivating the catalyst. This rationalizes the consistent lower activity observed for  $\text{Ni}_8\text{-TiO}_2\text{-r}$ .

Analysis of the kinetic network pinpoints the CO dissociation barrier playing a critical role in determining the overall activity and mechanistic route. To understand the underlying electronic effects leading to the difference in CO dissociation barrier between the anatase and rutile supported  $\text{Ni}_8$  clusters, a combined density of states and crystal orbital Hamilton population analysis was conducted. The integrated COHP value for the Ni–CO interaction at the Fermi level for the transition states for these two structures reveal that CO is more tightly bound to  $\text{Ni}_8$  supported on rutile as compared to a cluster supported on anatase. This is not caused by electronic metal support interactions but rather by the different morphology of the cluster. For  $\text{Ni}_8/\text{TiO}_2\text{-r}$ , the morphology allows for highly stable fivefold-coordinated CO whereas for  $\text{Ni}_8/\text{TiO}_2\text{-a}$ , only a fourfold-coordinated mode is available which leads to less strongly bound CO.

This study showcases the potential role the support has in affecting the preferred pathway, selectivity and activity of a catalyst by inducing a preferred morphology of adsorbed clusters.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Lulu Chen: conceptualization, data curation, formal analysis, investigation, validation, visualization, writing-original draft; Ying-Ying Ye: data curation, formal analysis, investigation,



visualization; Rozemarijn D. E. Krösschell: data curation, formal analysis visualization; Emiel J. M. Hensen: conceptualization, supervision, writing-review & editing, funding acquisition; Ivo A. W. Filot: conceptualization, methodology, resource, visualization, supervision, writing-review & editing, funding acquisition.

## Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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