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# Adsorption of CO<sub>2</sub> on Heterostructures of Bi<sub>2</sub>O<sub>3</sub> Nanocluster-Modified TiO<sub>2</sub> and the Role of Reduction in Promoting CO<sub>2</sub> **Activation**

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ABSTRACT: The capture and conversion of CO<sub>2</sub> are of significant importance in enabling the production of sustainable fuels, contributing to alleviating greenhouse gas emissions. While there are a number of key steps required to convert CO<sub>2</sub>, the initial step of adsorption and activation by the catalyst is critical. Well-known metal oxides such as oxidized  $TiO_2$  or  $CeO_2$  are unable to promote this step. In addressing this difficult problem, a recent experimental work



shows the potential for bismuth-containing materials to adsorb and convert  $CO_{2}$ , the origin of which is attributed to the role of the bismuth lone pair. In this paper, we present density functional theory (DFT) simulations of enhanced  $CO_2$  adsorption on heterostructures composed of extended  $TiO_2$  rutile (110) and anatase (101) surfaces modified with  $Bi_2O_3$  nanoclusters, highlighting in particular the role of heterostructure reduction in activating CO2. These heterostructures show low coordinated Bi sites in the nanoclusters and a valence band edge that is dominated by Bi-O states, typical of the  $Bi^{3+}$  lone pair. The reduction of  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures can be facile and produces reduced  $Bi^{2+}$  and  $Ti^{3+}$  species. The interaction of  $CO_2$ with this electron-rich, reduced system can produce CO directly, reoxidizing the heterostructure, or form an activated carboxyl species  $(CO_2^{-})$  through electron transfer from the reduced heterostructure to  $CO_2$ . The oxidized Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructures can adsorb CO<sub>2</sub> in carbonate-like adsorption modes, with moderately strong adsorption energies. The hydrogenation of the nanocluster and migration to adsorbed CO<sub>2</sub> is feasible with H-migration barriers less than 0.7 eV, but this forms a stable COOH intermediate rather than breaking C-O bonds or producing formate. These results highlight that a reducible metal oxide heterostructure composed of a semiconducting metal oxide modified with suitable metal oxide nanoclusters can activate  $CO_{22}$ potentially overcoming the difficulties associated with the difficult first step in CO<sub>2</sub> conversion.

# **1. INTRODUCTION**

Increasing energy demand is leading to fossil fuel supply issues, and the use of fossil fuels has pushed the atmospheric CO<sub>2</sub> concentration to 410 ppm. Continuing CO<sub>2</sub> emissions are projected to result in a higher than 2 °C rise in average global temperatures. Given these severe societal problems, there is an urgent need to find materials that can convert the CO<sub>2</sub> produced by the combustion of fossil fuels back to the fuels or to the precursors for the production of more useful chemicals. This will reduce our reliance on nonsustainable fossil fuels and contribute to curbing anthropogenic CO<sub>2</sub> emissions. The solar-driven photoreduction or thermal reduction of CO<sub>2</sub> to CO or directly to liquid fuels will enable a sustainable approach to producing fuels and storing solar energy in high-energy chemical bonds.<sup>1-11</sup>

Using solar energy, for example, through solar concentrators, coupled with catalysts that can promote activation of CO<sub>2</sub> to drive the CO<sub>2</sub> reduction process, is an attractive strategy to meet this ambitious aim. However, to date, there are no practical catalysts that can exploit solar energy to efficiently reduce CO<sub>2</sub> to useful chemical species. A range of different catalysts for CO<sub>2</sub> conversion using electrocatalysis, thermochemical catalysis, and photocatalysis has been investigated in recent years, and an example of such a photocatalyst is Ptmodified TiO<sub>2</sub> nanotubes.<sup>8,12,13</sup> However, the efficiencies for methane production are extremely low, and Pt will never be an economically viable catalyst for large-scale CO<sub>2</sub> conversion.

Irrespective of how electrons are provided to reduce CO<sub>2</sub>, the key step in any CO<sub>2</sub> capture and use/conversion process is the initial adsorption of CO<sub>2</sub>, which should promote the "activation" of the molecule. This activation can be a charge transfer to CO<sub>2</sub>, distortions to the molecular structure such as bending of O-C-O away from the linear elongations in the molecular C-O distances, or hydrogenation. CO<sub>2</sub> should either dissociate to a CO molecule or undergo hydrogenation to produce methane or methanol, via formate or carboxyl pathways. The activation should also avoid the production of overstabilized inactive surface-bound carbonates which would poison the catalyst.

In recent years, catalysts based on metallic Cu, oxide-derived Cu, or Cu with mixed oxidation states have gained great interest and have been demonstrated to reduce  $CO_2$  to useful molecules such as methane, methanol, or ethanol.<sup>14–22</sup> Recent experimental work indicates the ability of nanocatalysts

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containing a mix of Cu<sup>+</sup> and Cu<sup>2+</sup> oxidation states and in oxide-like structures to promote  $CO_2$  reduction<sup>1,2,10,14-16,18,19,21-29</sup> and this includes Cu metal, oxidederived Cu, and mixed oxidation state Cu. Modeling the interaction of CO<sub>2</sub> with copper oxides using density functional theory (DFT) has provided useful results for further development of catalysts for CO<sub>2</sub> conversion. Wu et al. studied the adsorption of  $CO_2$  at the  $Cu_2O(111)$  surface in which excess electrons were produced through the formation of oxygen vacancies<sup>18</sup> and found that dissociative adsorption of  $CO_2$  was thermodynamically unfeasible, and although a  $CO_2^{\delta-1}$ anion could be formed, this was not favorable, and hence excess electrons are not necessarily sufficient to promote CO<sub>2</sub> capture and conversion. Wu et al. also studied the adsorption of CO<sub>2</sub> and its derivatives at Cu<sub>2</sub>O(111) using hybrid  $\overline{DFT}^{21}$ and found that only the adsorption of linear CO<sub>2</sub> was favorable. This is supported by the work of Benavid and Carter who showed that physisorption of linear CO<sub>2</sub> is favored over adsorption of bent anionic CO2.<sup>19</sup> Mishra and colleagues reported strong CO<sub>2</sub> chemisorption at the high-energy Cu-Oterminated (110) surface of  $Cu_2O^{15}$  and exothermic adsorption of CO<sub>2</sub> at the high-energy (011) surface of CuO.<sup>2</sup> Uzunova et al. studied the conversion of CO<sub>2</sub> to methanol on Cu<sub>2</sub>O nanolayers and clusters<sup>16</sup> using hybrid DFT. The authors considered water as the source of H atoms for the hydrogenation of CO<sub>2</sub> and described a reaction pathway from a carboxyl group (\*COOH) to formic acid, which was the rate-limiting step, and then onto formaldehyde and finally methanol. This work would suggest other pathways for CO<sub>2</sub> conversion beyond the dissociation into CO. In the work of Favaro et al.,<sup>24</sup> a model of Cu with subsurface oxygen was required for copper to adsorb CO2 in the first place and understand the experimental findings. However, despite these advances, there still remains an urgent need from both a fundamental and a technoeconomic perspective to discover new materials that can activate and reduce CO<sub>2</sub>, in particular to produce sustainable fuels, particularly if renewable energy can be used, either for electroreduction or to produce renewable hydrogen from water.

Another popular metal oxide is titanium dioxide, and the adsorption of CO<sub>2</sub> at different titania surfaces and nanostructures has been widely studied. The roles of excess electrons introduced by oxygen vacancies, low coordinated atomic sites, and the surface structure in CO2 adsorption and activation have been discussed.<sup>30-32</sup> The presence of excess electrons and holes was shown to influence the adsorption and activation of  $CO_2$  at rutile (110), and both bent  $CO_2^-$  anion and  $CO_2^+$ cation configurations were identified from the DFT calculations.<sup>33</sup> Lee and Kanai<sup>32</sup> used DFT to explore the difference between anatase (101) and a nanostructured  $TiO_2$  quantum dot for CO<sub>2</sub> activation and hydrogenation. They found that the TiO<sub>2</sub> quantum dot promoted CO<sub>2</sub> activation and hydrogenation when compared to the extended anatase (101) surface. Yang and colleagues showed that subnanometer Pt clusters supported on the anatase (101) surface enhanced CO<sub>2</sub> activation through the provision of additional adsorption sites and the transfer of electron density to the TiO<sub>2</sub> substrate.<sup>34</sup>

Various other metal oxides have been investigated for  $CO_2$  conversion, and several theoretical studies have been conducted into the reaction pathways involving the hydrogenation of CO and  $CO_2$  at a variety of catalytic surfaces, including Cu/CeO<sub>2</sub> and Cu/CeO<sub>2</sub>/TiO<sub>2</sub><sup>17</sup> or Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.<sup>35</sup> An enhanced photoreduction of CO<sub>2</sub> with H<sub>2</sub>O

vapor has been reported for dispersed  $CeO_2/TiO_2$ .<sup>36</sup> Here, the ceria is modeled as a small cluster supported on rutile  $TiO_2$ , similar to the work on water gas shift,<sup>37–39</sup> and the role of  $Ce^{3+}$  in visible light absorption, photogenerated charge separation, and strengthening of the  $CO_2$ –surface bonding was highlighted.

Recent experimental works from Rosenthal and co-workers<sup>40-43</sup> and Walker et al.<sup>44</sup> strongly suggest that nontransition-metal based catalysts, in particular those containing bismuth or tin, are able to activate CO<sub>2</sub> or convert it to other molecules with good efficiency. The catalysts in refs<sup>40,43</sup> are composed of Bi–glassy carbon and use ionic liquids or Bi nanoparticles, which have large amounts of Bi<sup>3+</sup>. The former materials can convert CO<sub>2</sub> to alcohols with high efficiency, and even though ionic liquids are used, the role of Bi in the catalyst remains crucial to promote the conversion of CO<sub>2</sub>.

The bismuth pyrochlore oxide  $Bi_2Ti_2O_7$  was studied in ref 44 and was shown to have high  $CO_2$  chemisorption capacity. In this system, low-energy ion scattering (LEIS) shows clearly that the surface layer is terminated by a bismuth oxide layer. This surface structure arises from the well-known stereochemical lone pair in  $Bi^{3+.45,46}$  By contrast, in the pyrochlore  $Y_2Ti_2O_7$ , there is no surface enrichment with  $Y^{3+}$  (lacking the lone pair). This Bi-oxide-terminated pyrochlore was examined for its capacity to adsorb and activate  $CO_2$  using infrared spectroscopy. The features in the infrared spectrum corresponding to the adsorbed  $CO_2$  were clearly present upon heating to 308 K.  $Y_2Ti_2O_7$ , by contrast, does not strongly adsorb  $CO_2$ . This suggests that the adsorption of  $CO_2$  arises from the presence of  $Bi^{3+}$  and a bismuth oxide surface layer in the pyrochlore surface.

From the studies in refs,<sup>40,44</sup> it is reasonable to propose that the presence of the Bi<sup>3+</sup> cation, with its stereochemically active lone pair, in a Bi-oxide structure will be active in promoting the interaction of Bi-containing oxides with  $CO_2$ . However, the mechanism of  $CO_2$  adsorption and conversion on Bi<sup>3+</sup>containing materials, as a good exemplar of the p-block metal oxides, needs to be further investigated, and this is one of the aims of this study.

Previously, we have used first-principles DFT simulations to design heterostructured materials which are composed of TiO<sub>2</sub> (rutile or anatase) surfaces modified with metal oxide nanoclusters. In our earlier work, the emphasis has been on new heterostructured materials with predicted visible light absorption<sup>47-59</sup> and reduced charge recombination.<sup>48-52,60</sup> We have recently studied the interaction of molecules, such as  $CO_2$ , with tin(II) oxide,<sup>47</sup> zirconia,<sup>47</sup> manganese oxide,<sup>63</sup> alkaline earth oxide,<sup>64</sup> and ceria<sup>65</sup> nanocluster-modified TiO<sub>2</sub> heterostructures. We have found that such nanoclustermodified  $TiO_2$  heterostructures can adsorb  $CO_{2}^{47}$  but that some heterostructures, such as reduced MnO<sub>x</sub>-TiO<sub>2</sub>, do not show favorable CO<sub>2</sub> adsorption, even though reduced cations are present.<sup>63</sup> There is still much work to be done to understand the factors that drive CO2 activation on metal oxides.

In the present paper, we take the ideas from the experimental work on  $CO_2$  activation on Bi-containing materials, the ability of nanostructures to activate  $CO_2$ , and the activity of nanocluster-modified  $TiO_2$  and use first-principles DFT to examine in detail the interaction and adsorption of  $CO_2$  at  $Bi_2O_3$  nanocluster-modified rutile and anatase  $TiO_2$ . We explore the role of the Bi-oxide' the low coordinated sites in nanoclusters and reduction of the  $Bi_2O_3$ -

 $TiO_2$  heterostructures in  $CO_2$  adsorption and activation. In some examples, we examine further interaction with hydrogen for the first steps in hydrogenation and formation of intermediates such as COOH or HCOO. The role of heterostructure reduction in  $CO_2$  activation is crucial, wherein the charge transfer from the reduced oxide heterostructure can result in the formation of a carboxylate or direct formation of CO.

### 2. METHODS

In the DFT computations, we follow our approach from previous work<sup>61</sup> and prepare heterostructures of  $Bi_2O_3$  nanoclusters supported on the extended low-energy rutile (110) and anatase (101) surfaces; although other rutile and anatase surfaces can be present in, for example, typical TiO<sub>2</sub> nanoparticles, these are the dominant surface facets and are well-studied.

All DFT computations use a three-dimensional periodic surface slab within the VASP code  $^{66-69}$  and a plane-wave basis set to describe the valence electrons. Projector-augmented wave potentials,<sup>70,71</sup> with 4, 5, 6, 4, and 1 valence electrons for Ti, Bi, O, C, and H, respectively, describe the core-valence electron interactions, and this setup was extensively tested in our earlier work on Bi<sub>2</sub>O<sub>3</sub>-modified TiO<sub>2</sub>.<sup>61</sup> The cutoff for the kinetic energy is 396 eV, and the exchange-correlation functional is the Perdew-Wang  $91^{72}$  approximation. A Monkhorst-Pack  $(2 \times 1 \times 1)$  k-point sampling grid is used. For consistency with our previous work, we apply the DFT + U approach<sup>73,74</sup> to describe the Ti 3d states, with a value of U = 4.5 eV. The convergence criteria for the electronic and ionic relaxations are 0.0001 eV and 0.02 eV/Å. Methfessel-Paxton smearing is used with  $\sigma = 0.1$  eV (also for the broadening of the peaks in the projected density of states). We use the Newton-Raphson relaxation algorithm, and all calculations are spin-polarized throughout, with no constraints on the spin.

The rutile (110) surface is terminated by twofold coordinated bridging O atoms, with threefold coordinated inplane oxygen atoms in the surface layer. In the same layer, the Ti atoms take fivefold and sixfold coordinations. The anatase (101) surface is characterized by twofold coordinated oxygen atoms terminating the surface layer, and the outermost Ti atoms are fivefold coordinated. Surface supercell expansions of  $(2 \times 4)$  and  $(4 \times 2)$  are employed for rutile and anatase, respectively, and the vacuum gap in all cases is 12 Å.

In forming these composite structures, we first relax the gasphase metal oxide nanoclusters and the unmodified rutile and anatase surfaces using the same computational setup described above. The oxide nanocluster modifier is adsorbed at the  $TiO_2$ surfaces in different configurations, and each of these are relaxed, as described in refs.<sup>48,57,61,75</sup> We selected the most stable  $Bi_2O_3$ -TiO<sub>2</sub> composites for the study of CO<sub>2</sub> activation in the present paper. We will use the term  $Bi_2O_3$ -TiO<sub>2</sub> throughout this paper to indicate the general  $Bi_2O_3$  nanocluster-modified  $TiO_2$  heterostructure, using the precise nanocluster composition and  $TiO_2$  surface when necessary.

The stability of the heterostructure is characterized by the computed nanocluster adsorption energy,  $E^{ads}$ 

$$E^{\text{ads}} = E[(\text{Bi}_2\text{O}_3)_n - \text{TiO}_2] - \{E[(\text{Bi}_2\text{O}_3)_n] + E[\text{TiO}_2]\}$$
(1)

where  $E[(Bi_2O_3)_n - TiO_2]$  is the computed total energy of the  $Bi_2O_3$  nanocluster-modified  $TiO_2$  surface (in which *n* is the number of  $Bi_2O_3$  units in the nanocluster, so that in this paper

n = 2 or 3),  $E[(Bi_2O_3)_n]$  is the computed total energy of the free  $(Bi_2O_3)_n$  nanocluster, and  $E[(TiO_2)]$  is the computed total energy of the unmodified TiO<sub>2</sub> (rutile/anatase) surface.

The reduction of the  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures is studied by removing oxygen from the nanocluster modifier (which is always more stable than removing oxygen from the TiO<sub>2</sub> support) and computing the formation energy of the oxygen vacancy as follows

$$E^{\text{vac}} = E\{((\text{Bi}_2\text{O}_{3-x})_n - \text{Ti}\text{O}_{2-x}) + 1/2E(\text{O}_2)\} - E((\text{Bi}_2\text{O}_3)_n - \text{Ti}\text{O}_2)$$
(2)

where  $E\{((Bi_2O_{3-x})-TiO_2)$  is the total energy of the  $Bi_2O_3-TiO_2$  composite with one oxygen removed and  $1/2E(O_2)$  is the reference energy for oxygen, namely half the total energy of the  $O_2$  molecule. We correct the oxygen vacancy formation energy for entropy, which, at 298 K, is 0.60 eV. Despite the known errors in the DFT energy of the reference  $O_2$  molecule, the *trends* in oxygen vacancy formation are independent of this error. We also use ab initio thermodynamics to determine the stability of the reduced  $Bi_2O_3-TiO_2$  heterostructures formed by removing oxygen over a range of temperatures.

To analyze the stability of the reduced heterostructured models when exposed to an environment of oxygen, we use the DFT-derived total energies as an input into an atomistic thermodynamics framework, which considers the effect of the surrounding gas phase as a reservoir that is in thermodynamic equilibrium with the heterostructure. If we assume that the oxygen reservoir exchanges particles with the system without affecting its chemical potential, the oxygen vacancy formation energy is calculated as follows

$$E^{\text{vac}} = [E(\text{Bi}_2\text{O}_{3-\delta} - \text{TiO}_2) + N_0\mu_0(p, T)] - E(\text{Bi}_2\text{O}_3 - \text{TiO}_2)$$
(3)

where  $E(\text{Bi}_2\text{O}_{3-\delta}-\text{TiO}_2)$  and  $E(\text{Bi}_2\text{O}_3-\text{TiO}_2)$  are the total DFT energies of the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructures with and without the oxygen vacancy,  $N_{\text{O}}$  is the number of oxygen atoms removed, and  $\mu_{\text{O}}(p,T)$  is the chemical potential of oxygen. Approximating oxygen as an ideal gas, we explicitly introduce pressure and temperature in our model through the analytic relation between the chemical potentials and the temperature and pressure of the two gas reservoirs as follows

$$\mu_{\rm O}(p, T) = \left[\frac{1}{2}E_{\rm O_2} + \mu_{\rm O_2}' + k_{\rm B}T \ln\left(\frac{p_{\rm O_2}}{p^0}\right)\right] \tag{4}$$

Here, *T* and *p* represent the temperature and partial pressure of oxygen,  $p^0$  denotes atmospheric pressure, and  $k_{\rm B}$  is the Boltzmann constant.  $\mu'$  is the energetic term that includes contributions from the rotations and vibrations of the molecule, as well as the ideal-gas entropy at 1 atm, which can be calculated or taken from the experimental values listed in the thermodynamic tables. Thus, for a given pressure, the stability of oxygen vacancies can be determined over a range of temperatures.

The CO<sub>2</sub> adsorption energy at  $Bi_2O_3$ -modified  $TiO_2$  heterostructures is defined in eq 5

$$E^{ads} = E(CO_2@(Bi_2O_3)_n - TiO_2) - \{E((Bi_2O_3)_n - TiO_2) + E(CO_2)\}$$
(5)

Figure 1. Relaxed atomic structure for  $Bi_2O_3$  nanocluster-modified rutile (110) and anatase (101). (a)  $Bi_4O_6$ -rutile (110), (b)  $Bi_6O_9$ -rutile (110), and (c)  $Bi_4O_6$ -anatase (101). The color coding in this and subsequent figures is Ti = light gray sphere, O = red sphere, and Bi = purple sphere. Bi and O atoms in the adsorbed nanoclusters are depicted by larger radius spheres.



**Figure 2.** PEDOS projected onto the Bi 6s, Ti 3d, and O 2p states (nanocluster and surface) for (a)  $Bi_4O_6$  rutile (110), (b)  $Bi_6O_9$ -rutile (110), and (c)  $Bi_4O_6$ -anatase (101). The zero of energy in all cases is the Fermi level. The left panels show the cation PEDOS and the right panels show the oxygen 2p PEDOS.

where  $E(CO_2@(Bi_2O_3)_n-TiO_2)$  is the computed total energy of the relaxed adsorption structure of CO<sub>2</sub> at Bi<sub>2</sub>O<sub>3</sub>-modified TiO<sub>2</sub> composites, whether stoichiometric or reduced. We examined many CO<sub>2</sub> adsorption structures, and those shown in the following text are the most stable that we have found. Although van der Waals corrections can be added to these computations, we have tested and found that the change in the adsorption energies is ca. 0.15 eV, which is not significant compared to the magnitude of the computed CO<sub>2</sub> adsorption energies, and furthermore, there is no effect of the inclusion of vdW corrections on the relative stability of different CO<sub>2</sub> adsorption structures.

## 3. RESULTS AND DISCUSSION

**3.1.**  $Bi_2O_3$ -Modified Rutile and Anatase TiO<sub>2</sub> Heterostructures. Figure 1 shows the atomic structures of the nanocluster-modified anatase (101) and rutile (110) surfaces of  $Bi_4O_6$  and  $Bi_6O_9$ . We have described these heterostructured systems in detail in previous work,<sup>61</sup> and we briefly summarize the key features required for this paper. The adsorption energies can be computed relative to the corresponding gasphase stoichiometric  $Bi_2O_3$  nanoclusters, and these are -5.18, -5.18, and -5.72 eV for  $Bi_4O_6$ -rutile,  $Bi_6O_9$ -rutile, and  $Bi_4O_6$ anatase, respectively. If we consider these energies in terms of the deposition of the nanoclusters at very low loading/ coverage through atomic layer deposition, chemisorption– calcination, or incipient wetness impregnation, then the above energies can be related to the desorption of the  $Bi_2O_3$ nanoclusters from the  $TiO_2$  supports. The magnitude of the computed energies indicates a strong binding of the nanocluster modifiers at both  $TiO_2$  surfaces and suggests they would only desorb at very high temperatures.

We can also consider the stability against sintering into larger nanoclusters. In the gas phase, the gain in energy when two nanoclusters of composition  $Bi_2O_3$  coalesce into a larger  $Bi_4O_6$  nanocluster is -6.1 eV, and the coalescence of a gasphase  $Bi_2O_3$  and a gas-phase  $Bi_4O_6$  nanocluster results in a gain of 3.1 eV. On the surface, we use the total energies of the bismuth oxide nanocluster-modified rutile heterostructures to assess the nanocluster stability against coalescence into larger



**Figure 3.** Atomic structure and spin density isosurfaces of the most stable reduced  $Bi_2O_3$ - $TiO_2$  heterostructures: (a)  $Bi_4O_6$ -rutile (110), (b)  $Bi_6O_9$ -rutile (110), and (c)  $Bi_4O_6$ -anatase (101). Spin density isosurfaces enclose spin densities up to 0.02 electrons/Å<sup>3</sup>. The color coding of the atoms is the same as in Figure 1.

nanoclusters.<sup>75</sup> For the example of  $Bi_2O_3$  and  $Bi_4O_6$  coalescing to a  $Bi_6O_9$  nanocluster

$$\Delta E = (E^{\text{Bi}_6\text{O}_9\text{-rutile}} + E^{\text{rutile}(110)})$$
$$- (E^{\text{Bi}_2\text{O}_3\text{-rutile}} + E^{\text{Bi}_4\text{O}_6\text{-rutile}})$$

The computed energy is +2.69 eV against coalescence of the two smaller nanoclusters supported on rutile (110). Thus, when the Bi<sub>2</sub>O<sub>3</sub> nanoclusters are supported on rutile or anatase, they will be stable against desorption or aggregation. The high stability of the supported Bi<sub>2</sub>O<sub>3</sub> nanoclusters is primarily driven by the formation of new interfacial bonds between the nanocluster and the surface. We also note that the extensive work of Graciani et al. on ceria–TiO<sub>2</sub> used small Ce<sub>2</sub>O<sub>3</sub> species supported on rutile (110),<sup>38,39</sup> which were also shown to be highly stable.

On Bi<sub>4</sub>O<sub>6</sub>-rutile, two Bi cations bind to the bridging surface oxygen, with typical Bi–O distances of 2.17 Å. These Bi cations are threefold coordinated, whereas the remaining Bi cations are twofold coordinated. Three oxygen atoms from the nanocluster bind to the fivefold coordinated Ti surface atoms, with the Ti–O distances in the range of 1.83–2.05 Å. In the Bi<sub>6</sub>O<sub>9</sub>-rutile nanocluster, one Bi cation binds to a bridging oxygen, with a Bi–O distance of 2.37 Å. Two oxygen atoms from the nanocluster bind to the surface Ti atoms, with the Ti–O distances of 1.94 and 1.86 Å. Here, the terminal Bi cations, furthest away from the cluster–surface interface, are threefold coordinated, and there are twofold coordinated oxygen sites in the nanocluster.

In  $Bi_4O_6$ -anatase, three Bi cations bind to the surface oxygen, with the Bi–O distances of 2.14, 2.14, 2.24, and 2.17 Å. The two Bi cations furthest away from the cluster–surface interface are threefold coordinated and the remaining Bi cations are fourfold coordinated. Four oxygen atoms in the nanocluster bind to the surface Ti, with the distances Ti–O in the range of 1.87–2.06 Å. There are three twofold coordinated oxygen sites: one is the terminal oxygen in the nanocluster and the remaining two sites bridge the nanocluster and the anatase (101) surface.

The other important aspect of the  $Bi_2O_3$ -TiO<sub>2</sub> composites for the interaction with CO<sub>2</sub> is their electronic properties, and in Figure 2 we show the projected electronic density of states (PEDOS) for the  $Bi_2O_3$ -rutile and  $Bi_2O_3$ -anatase systems.  $Bi^{3+}$ is an interesting species as it has a stereochemically active lone pair, which results in the presence of Bi-derived electronic states at the top of the valence band. This gives rise to the distorted structure of bulk  $Bi_2O_3^{46}$  and the Bi-rich surface region in the pyrochlore  $Bi_2Ti_2O_7$ .<sup>44</sup> The other metal oxides with +3 cations do not show these structural distortions.

In the PEDOS of the  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures, the Bi electronic states are present at the valence band edge of all the

composite systems studied. For modified rutile (110), we see Bi (6s + 6p) and O 2p states originating from the nanoclusters lying at a higher energy than the corresponding  $TiO_2$  valence and conduction band edges, which should result in a small red shift in light absorption. For anatase, the  $Bi_2O_3$ -derived states lie just below the anatase valence band edge, which results in no predicted red shift. The key finding is that the Bi states lie at the top of the valence band edge, and this can be important in the reduction or  $CO_2$  adsorption on the  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures.

Finally, we present the results for the reduction of the  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures. The reduced heterostructures are prepared by removing oxygen atoms from the Bi<sub>2</sub>O<sub>3</sub> nanoclusters and computing the oxygen vacancy formation energy. From a practical perspective, reduction can be facilitated by a thermochemical process using concentrated solar radiation or by the introduction of hydrogen in a redox process. Relaxing the structure after the removal of oxygen, the most stable reduced heterostructures are shown in Figure 3. The computed formation energies for the most stable oxygen vacancy sites are 1.75 eV (1.12 eV) for  $Bi_4O_6$ -rutile (110), 1.64 eV (1.01 eV) for  $Bi_6O_9$ -rutile (110), and 3.0 eV (2.37 eV) for  $Bi_4O_6$ -anatase (101), where the formation energies corrected for  $T\Delta S$  at 298 K are given in parentheses. These formation energies that show a moderate cost for oxygen vacancy formation in the supported Bi2O3 nanoclusters are notably smaller than that on the corresponding bare  $TiO_2$  surfaces (3.5) eV for rutile (110) and 3.6-4.1 eV for anatase (101)<sup>76</sup>), so that reduction should be possible under moderate conditions. The other oxygen sites have formation energies larger than 2 eV on Bi<sub>4</sub>O<sub>6</sub>-rutile and between 3.4 and 3.7 eV on Bi<sub>4</sub>O<sub>6</sub>anatase. Figure 4 shows the stability of the most stable oxygen vacancy sites in each heterostructure as a function of temperature at a pressure of 1 atm. From this plot, we can



**Figure 4.** Computed oxygen vacancy formation energy for  $Bi_2O_3$ -modified TiO<sub>2</sub> as a function of temperature at a pressure of 1 atm.



**Figure 5.** Atomic structure of the most stable  $CO_2$  adsorption structures on reduced  $Bi_2O_3$ -TiO<sub>2</sub> composites: (a)  $Bi_4O_6$ -rutile (110), (b)  $Bi_6O_9$ -rutile (110), and (c)  $Bi_4O_6$ -anatase (101). The color coding is the same as in Figure 1, with an additional inclusion of a gray sphere for carbon. The Bi and O atoms in the supported  $Bi_2O_3$  nanoclusters are depicted with larger diameter spheres.

see that reduction should take place at 500-600 K, which is certainly feasible in the context of CO<sub>2</sub> reduction/conversion processes. For the rutile-supported Bi<sub>6</sub>O<sub>9</sub> nanocluster, the larger formation energy of the vacancy clearly results in a higher temperature for vacancy formation, although this is still notably lower than that on bare rutile (110).

After the reduction of the  $Bi_2O_3$  nanoclusters, the local atomic structure shows some changes. On  $Bi_4O_6$ -rutile (110), the removal of oxygen results in the formation of a structure that shows symmetry, with two twofold coordinated oxygen atoms terminating the nanocluster. The Bi cations are threefold coordinated, and each Bi atom binds to a bridging oxygen atom from the rutile (110) surface, with the Bi–O distances in the range of 2.17–2.18 Å. Furthermore, each Bi atom also coordinates to one oxygen from the nanocluster, which itself binds to a surface Ti atom, with the Bi–O distances of 2.07–2.15 Å and Ti–O distances of 2.03 Å.

On  $Bi_6O_9$ -rutile, the formation of the most stable oxygen vacancy results in small changes to the nanocluster structure. Two Bi cations are coordinated to the surface-bridging oxygen sites, with the Bi–O distances of 2.20–2.23 Å. Two nanocluster oxygen bind to the surface fivefold coordinated Ti, with the Ti–O distances of 1.89 and 2.02 Å, whereas after relaxation, four oxygen atoms take a twofold coordination environment by breaking the bonds with Bi cations (giving long Bi–O distances of 2.51 and 2.56 Å).

On Bi<sub>4</sub>O<sub>6</sub>-anatase, two Bi cations are threefold coordinated and the remaining cations are fourfold coordinated. The typical Bi–O distances range from 1.86 to 2.15 Å, and the Bi–O distances to the surface range from 2.12 to 2.16 Å. One oxygen atom from the surface migrates outward to bind to a Bi cation in the nanocluster, with three oxygen atoms in the nanocluster binding to the surface Ti sites; the Bi–O distances are in the range 1.86–1.90 Å.

The localization of the two electrons released upon removal of the neutral oxygen atom is shown by the spin density isosurfaces in Figure 3. For both  $Bi_2O_3$  nanocluster-modified rutile (110) composites, the electrons preferentially localize on the Ti sites in the rutile (110) surface, with the computed Ti Bader charges of +1.65/1.71 electrons in  $Bi_4O_6$ -rutile and +1.65/1.69 electrons in  $Bi_6O_9$ -rutile and spin magnetization in the range 0.92–0.94  $\mu_B$ . For reference, Ti<sup>4+</sup> cations have computed Bader charges of +1.30 electrons and zero spin magnetization. The first electron localizes on a subsurface Ti site and the second electron localizes onto a surface fivefold coordinated Ti site that has no interaction with the supported nanocluster. These values are typical of the reduced Ti<sup>3+</sup> species in rutile (110).

In contrast, on  $\text{Bi}_4\text{O}_6$ -anatase (101), the two electrons localize on a surface fivefold coordinated  $\text{Ti}^{3+}$  site and on a Bi site in the nanocluster, which results in the formation of a reduced Bi<sup>2+</sup> species. The computed Bader charges are +1.74 electrons on Ti and +2.99 electrons on Bi; the latter is comparable to a computed Bi Bader charge of +2.1 electrons for Bi<sup>3+</sup> cations, indicating the reduction of the Bi species. The computed spin magnetizations on Ti and Bi are 0.96 and 0.7  $\mu_{\rm B}$ . This Bi site binds to the oxygen that migrated out of the surface, and this particular oxygen bridges the two reduced Ti<sup>3+</sup> and Bi<sup>2+</sup> sites.

**3.2.** Adsorption of CO<sub>2</sub> at Reduced  $Bi_2O_3-TiO_2$ Heterostructures. We now discuss the adsorption of CO<sub>2</sub> at the  $Bi_2O_3$  nanocluster-modified TiO<sub>2</sub> heterostructures, and in this section we focus on the reduced heterostructures. We examined the interaction of the reduced  $Bi_2O_3-TiO_2$ heterostructures with CO<sub>2</sub> in a number of adsorption configurations. Figure 5 shows the most stable relaxed structures after the relaxation of adsorbed CO<sub>2</sub> on each reduced  $Bi_2O_3-TiO_2$  heterostructure. The computed interaction energies for CO<sub>2</sub> are -0.45 eV on reduced  $Bi_4O_6$ -rutile (110), -0.53 eV on reduced  $Bi_6O_9$ -rutile (110), and -0.93 eV on reduced  $Bi_4O_6$ -anatase (101). These energies indicate a moderately strong interaction between the initially reduced metal oxide heterostructure and the CO<sub>2</sub> molecule.

 $CO_2$  binds to reduced Bi<sub>4</sub>O<sub>6</sub>-rutile (110) with the formation of two Bi–O bonds, with the Bi–O distances of 2.45 and 2.52 Å. The carbon of CO<sub>2</sub> binds to the oxygen in the nanocluster, with a C–O distance of 1.38 Å. The C–O distances in the adsorbed CO<sub>2</sub> are elongated to 1.27 Å, and the O–C–O angle is 130°. Thus, the CO<sub>2</sub> molecule adsorbs moderately exothermically on the reduced supported Bi<sub>4</sub>O<sub>6</sub> nanocluster in a manner that can be considered carbonate-like with a tridentate adsorption configuration, although one of the C–O bonds is significantly longer than the typical C–O carbonate distance.

Examining the electronic structure in the  $CO_2$ -Bi<sub>4</sub>O<sub>6</sub>-rutile system, the computed Bader charges on the previously reduced Ti atoms are now +1.3 electrons, signifying the presence of oxidized Ti<sup>4+</sup> species. Interestingly, we find that the charge on two Bi cations in the nanocluster changes to 2.8 and 3.2 electrons, indicating that these Bi cations are partially reduced. One of these Bi cations binds to the oxygen of CO<sub>2</sub>, suggesting a rearrangement of charge upon CO<sub>2</sub> adsorption.

On  $Bi_6O_9$ -rutile (110), the relaxation of initially adsorbed  $CO_2$  leads to spontaneous breaking of a C–O bond in the molecule, which results in the release of a free CO molecule, with no energy barrier to this process. Although one might expect a significant energy gain in breaking a C–O bond, we

have to consider that this process heals the vacancy site on the  $Bi_2O_3$  nanocluster, which has a high stability, and there would also be an energy cost to break the C–O bond in the molecule. In any case, the key point is the exothermic release of CO.

When CO is released, the previous supported  $Bi_6O_8$ nanocluster is reoxidized, with the  $Bi_6O_9$  composition. Examining the atomic structure, we see that the free CO has a C–O distance of 1.14 Å, which is typical of the gas-phase CO, and the Bi–O distances are similar to those in the stoichiometric  $Bi_6O_9$ -rutile system. In the  $Bi_6O_9$ -rutile system, the computed Bader charges of Ti and Bi are +1.3 and +2.2 electrons, consistent with the presence of only oxidized Ti<sup>4+</sup> and Bi<sup>3+</sup> species. The electrons on the TiO<sub>2</sub> surface after reduction are therefore transferred to CO<sub>2</sub> to allow the formation of new Bi–O bonds and a free CO molecule.

To examine this in more detail and complete a redox cycle, we adsorb  $H_2$  at the site of the oxygen species that results from  $CO_2$  dissociation, that is, oxygen that reoxidized reduced  $Bi_6O_8$ -rutile. Upon relaxation, a water molecule spontaneously forms, with an exothermic energy gain of 1.13 eV which reduces the  $Bi_6O_9$  nanocluster; removal of water from the supercell requires 0.43 eV, and the reduced supported nanocluster is available for reaction with another  $CO_2$ . Thus, the  $Bi_6O_9$  nanocluster supported on rutile  $TiO_2$  appears to show a pathway for  $CO_2$  dissociation through a redox process involving water formation in a reverse water gas shift-like process.

Finally, on  $Bi_4O_6$ -anatase (101), the computed Bader charges on the CO<sub>2</sub> molecule indicate a charge transfer of ca. 1.5 electrons to the molecule from the reduced composite. The computed Bader charges of 1.3 and 2.1 electrons on previously reduced Ti and Bi further support this electron transfer, which reoxidises Ti and Bi. This process then results in the formation and stabilization of a carboxyl,  $CO_2^-$  species. This is one of the activated CO<sub>2</sub> species that is important in CO<sub>2</sub> conversion. In the gas phase, the potential required for the formation of  $CO_2^{-}$  is prohibitively high, but in the reduced Bi<sub>2</sub>O<sub>3</sub>-modified anatase system, the presence of both low coordinated active sites and excess electrons after reduction appears to facilitate electron transfer to the adsorbed CO<sub>2</sub> molecule. In adsorbed carboxyl, the C-O distances are 1.25 and 1.27 Å, again showing a significant elongation over the free molecule. The bending of CO2 upon interaction with the nanocluster is also apparent, with an O-C-O angle of  $130^{\circ}$ . CO<sub>2</sub> binds to the nanocluster through a Bi–O bond, which has a distance of 2.42 Å and a Bi-C bond of 2.37 Å involving a second Bi atom in the nanocluster.

The computed vibrational frequencies for CO<sub>2</sub> adsorbed on reduced heterostructures are shown in Table 1. The computed gas-phase vibrational modes of CO<sub>2</sub> are 2354, 1325, and 632 cm<sup>-1</sup>, with the latter being degenerate. These correspond to the asymmetric C=O stretch, the symmetric C=O stretch, and the O-C-O bending mode. The large red shift in the C=O stretching mode of 760 and 767 cm<sup>-1</sup> on Bi<sub>4</sub>O<sub>6</sub>-rutile and Bi<sub>4</sub>O<sub>6</sub>-anatase is consistent with the strong adsorption of CO<sub>2</sub>, as is the breaking of the degeneracy in the CO<sub>2</sub> bending mode upon adsorption. We note that on Bi<sub>4</sub>O<sub>6</sub>-anatase the splitting of the degeneracy in the CO<sub>2</sub> bending mode is larger, the origin of which is likely due to one oxygen of CO<sub>2</sub> not binding with the Bi<sub>2</sub>O<sub>3</sub> nanocluster. By contrast, the two oxygen atoms in CO<sub>2</sub> bind with the nanocluster in Bi<sub>4</sub>O<sub>6</sub>-rutile, so that the split in the degeneracy of the two modes is smaller.

Table 1. Computed  $CO_2$  Vibrational Frequencies for Activated  $CO_2$  at Reduced  $Bi_2O_3$ -Ti $O_2^{a}$ 

reduced $Bi_2O_3$ -Ti $O_2$ heterostructure	$\rm CO_2$ vibrational frequencies/cm <sup>-1</sup>				
Rutile (110)					
Bi <sub>4</sub> O <sub>6</sub> -rutile (110)	1594, 1254, 941, 774				
Bi <sub>6</sub> O <sub>9</sub> -rutile (110)	gas-phase CO				
Anatase (101)					
Bi <sub>4</sub> O <sub>6</sub> -anatase (101)	1587, 1203, 700, 531				
<sup>a</sup> Our computed vibrational frequence	cies of free CO <sub>2</sub> are 2354, 1325,				

and 632 cm<sup>-1</sup>, which can be compared with the experimental data: 2349 cm<sup>-1</sup> (C=O asymmetric stretch), 1388 cm<sup>-1</sup> (C=O symmetric stretch), and 667 cm<sup>-1</sup> (C=O bonding, degenerate).

In addition to the excess electrons introduced by reduction and the presence of Bi–O electronic states at the top of the valence band, the atomic structure of the supported  $Bi_2O_3$ nanoclusters can facilitate  $CO_2$  adsorption because of the presence of low coordinated atomic sites and the flexibility in these supported nanoclusters that allows strong relaxations after the adsorption of molecules. We can also relate these findings to the work of Walker et al.<sup>44</sup> on the Bi-containing pyrochlore. In this system, the surface is terminated by a Bi–O layer, similar to our Bi<sub>2</sub>O<sub>3</sub> nanocluster-modified TiO<sub>2</sub>, and the Bi 6s/6p electronic states are mixed with O 2p states at the top of the valence band. Thus, the pyrochlore has a suitable electronic structure to permit interaction with  $CO_2$  and an atomic structure that also facilitates the interaction with  $CO_3$ .

Given that the adsorption of  $CO_2$  is the crucial first step in the catalytic conversion of  $CO_2$ , which is generally not favorable or could form highly stable carbonates on metal oxides, our finding that  $CO_2$  interacts moderately strongly with the reducible  $Bi_2O_3$ -modified  $TiO_2$  and can form CO or a carboxyl intermediate is a key result of this work.

3.3.  $CO_2$  Adsorption at Oxidized  $Bi_2O_3$ -TiO<sub>2</sub> Heterostructures. Table 2 presents the computed adsorption

Table 2. Computed Adsorption Energies, in eV, of  $CO_2$  at  $Bi_2O_3$ -Modified Rutile (110) and Anatase (101) Heterostructures

adsorption configuration	$E^{\rm ads}/{ m eV}$			
On Rutile (110)				
$Bi_4O_6$ -rutile (110) + $CO_2$	-0.37			
$Bi_4O_6$ -rutile (110) + $CO_2$	-0.54			
$Bi_6O_9$ -rutile (110) + $CO_2$ (linear)	-0.28			
$Bi_6O_9$ -rutile (110) + $CO_2$	-1.01			
On Anatase (101)				
$Bi_4O_6$ -anatase (101) + $CO_2$ (linear)	-0.51			
$Bi_4O_6$ -anatase (101) + $CO_2$	-0.82			

energies of the two most stable adsorption configurations of  $CO_2$  at each oxidized  $Bi_2O_3$ -TiO<sub>2</sub> heterostructure, and Figure 6 shows the relaxed atomic structures for these  $CO_2$  adsorption configurations. From Table 2, we can see that there is at least one moderately strong interacting  $CO_2$  adsorption configuration at each  $Bi_2O_3$ - TiO<sub>2</sub> heterostructure, with the computed adsorption energies of -0.54, -1.01, and -0.82 eV on  $Bi_4O_6$ -rutile,  $Bi_6O_9$ -rutile, and  $Bi_4O_6$ -anatase, respectively. Compared to the computed adsorption energies of  $CO_2$  on other oxidized metal oxide-modified TiO<sub>2</sub> systems, for example, in ref 47 or on polymorphs of TiO<sub>2</sub> itself,  $^{10,30,31}$  the adsorption energies of  $CO_2$  on  $Bi_2O_3$ -modified TiO<sub>2</sub> are



**Figure 6.** Relaxed adsorption structures of  $CO_2$  at  $Bi_2O_3$ -modified rutile (110) and anatase (101) composites; the composition is indicated in each case. (a,b)  $CO_2$  adsorption at  $Bi_4O_6$ -rutile (110) (c,d)  $CO_2$  adsorption at  $Bi_6O_9$ -rutile (110), and (e,f)  $CO_2$  adsorption at  $Bi_4O_6$ -anatase (101). The color coding is the same as in Figure 3.

notably stronger, indicating that these heterostructures are more favorable toward  $CO_2$  adsorption, although we note that there is no direct formation of CO or carboxylate, suggesting that the oxidized  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures may facilitate  $CO_2$  capture.

Examining the atomic structures for the adsorbed  $CO_2$ , we see that there are adsorption configurations on  $Bi_6O_9$ -rutile and  $Bi_4O_6$ -anatase, namely the configurations in Figure 6c,e, which have the weakest interactions and show a *linear*  $CO_2$  that is unchanged from the gas phase. This is a  $CO_2$  physisorption mode, which we do not expect to be important.

The other adsorption modes in Figure 6 are of more interest, and these show new C–O interactions with the supported nanoclusters, and the adsorption structure is consistent with a carbonate-like adsorption mode, albeit without the strong stabilization usually found for carbonate adsorption,<sup>64,65</sup> and consistent with the CO<sub>2</sub> adsorption on the Bi-oxide-terminated pyrochlore.<sup>44</sup>

Table 3 presents the important C–O distances, O–C–O bending angles, and the computed CO<sub>2</sub> vibrational modes. The common feature of these adsorption modes of CO<sub>2</sub> is that the molecule is clearly bent (gas-phase CO<sub>2</sub> is linear, with an O–C–O angle of 180°). The O–C–O angles in the adsorbed CO<sub>2</sub> are 131°, 127°, and 130° on Bi<sub>4</sub>O<sub>6</sub>-rutile, Bi<sub>6</sub>O<sub>9</sub>-rutile,

#### Table 3. Computed C–O and Bi–O Distances and $CO_2$ Vibrational Frequencies for $CO_2$ Adsorbed at $Bi_2O_3$ -Modified Rutile (110) and Anatase (101)<sup>*a*</sup>

structure	C−O/Å	O–C–O angle/°	$\rm CO_2$ vibrational frequencies/cm <sup>-1</sup>				
Rutile (110)							
$Bi_4O_6$ -rutile (110) + $CO_2$	1.27, 1.26, 1.39	131	1617, 1250, 924, 774				
$Bi_6O_9$ -rutile (110) + $CO_2$	1.26, 1.29, 1.39	127	1531, 1304, 1028, 774				
	Anatase (10)	l)					
$Bi_4O_6$ -anatase (101) + $CO_2$	1.26, 1.27, 1.39	130	1593, 1243, 917, 790				

<sup>*a*</sup>The first two C–O distances in column 2 are in the adsorbed molecule and the third C–O distance is to oxygen in the  $Bi_2O_3$  nanocluster. Our computed vibrational frequencies of free  $CO_2$  are 2354, 1325, and 632 cm<sup>-1</sup>, with the latter being degenerate.

and  $Bi_4O_6$ -anatase. This is consistent with the bending of activated  $CO_2$  observed on other materials, including transition-metal carbides, or on ceria-modified rutile (110).<sup>4,77,78</sup>

On Bi<sub>4</sub>O<sub>6</sub>-rutile, the C–O distances in the adsorbed CO<sub>2</sub> elongate to 1.26 and 1.27 Å, whereas the C–O distance to nanocluster oxygen is 1.39 Å. This is a notable elongation in the C–O distances over those in the gas-phase molecule (which is 1.16 Å). Similarly, on Bi<sub>6</sub>O<sub>9</sub>-rutile, the resulting bidentate adsorption configuration has elongated C–O distances of 1.26 and 1.29 Å in the molecule, whereas the C–O distance to the nanocluster is 1.39 Å. On Bi<sub>4</sub>O<sub>6</sub>-anatase, the carbon atom binds in a monodentate fashion to one oxygen in the nanocluster, with a C–O distance of 1.29 Å, whereas the C–O distances in the molecule are 1.26 and 1.27 Å.

Clearly, on Bi<sub>2</sub>O<sub>3</sub>-modified TiO<sub>2</sub>, although the CO<sub>2</sub> molecule does not adsorb in a typical carbonate adsorption mode in which the three C–O distances are equal (~1.29 Å) and the O–C–O angles are 120°, we can nonetheless describe the adsorption as carbonate-like. Although a new C–O interaction with a C–O distance of 1.39 Å is present, we can propose that this interaction participates in helping to stabilize the adsorbed CO<sub>2</sub>, so that it can further interact with hydrogen (see Section 3.3).

We have also computed the vibrational modes of adsorbed  $CO_2$  on  $Bi_2O_3$ -modified  $TiO_2$ . Upon the adsorption of  $CO_2$  at the oxidized  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures, there are significant red shifts in the asymmetric C=O stretch of 737, 823, and 761 cm<sup>-1</sup> on  $Bi_4O_6$ -rutile,  $Bi_6O_9$ -rutile, and  $Bi_4O_6$ -anatase, respectively. The degeneracy of the O-C-O bending mode is lifted upon adsorption at  $Bi_2O_3$ -TiO<sub>2</sub>. CO<sub>2</sub> adsorbed on  $Bi_6O_9$ -rutile shows the largest red shift of the C=O stretch, which is consistent with its larger adsorption energy and distortions away from the gas-phase  $CO_2$  geometry. This shift in the C=O stretching mode correlates with the strength of the  $CO_2$ - $Bi_2O_3$ -TiO<sub>2</sub> interaction, and it has been observed in the experimental studies of  $CO_2$  adsorption on a range of materials.<sup>79-81</sup>

Finally, we briefly examine the electronic structure. Figure 7 shows the PEDOS for C and O atoms in  $CO_2$ , and Ti and Bi atoms, as the examples of  $CO_2$  adsorbed on  $Bi_6O_9$ -rutile and  $Bi_4O_6$ -anatase. In both cases, the  $CO_2$ -derived C 2p and O 2p electronic states lie at the top of the valence band. Furthermore, there is a strong interaction between the Bi 6s/



Figure 7. PEDOS projected onto the Ti 3d, Bi 6s/6p, and  $CO_2$  2p states after the adsorption of  $CO_2$  onto (a)  $Bi_6O_9$ -rutile and (b)  $Bi_4O_6$ -anatase.

6p states and the carbon and oxygen 2p states of  $CO_2$ . This is consistent with the strong interaction and distortion of  $CO_2$ when adsorbed at the supported  $Bi_2O_3$  nanoclusters. We have also computed the Bader atomic charges upon  $CO_2$ adsorption. These do not show a significant charge transfer between  $Bi_2O_3$ -TiO<sub>2</sub> and  $CO_2$ , indicating that there is no charge transfer upon the adsorption of  $CO_2$ .

In understanding the strong  $CO_2$  adsorption without any significant charge transfer, we consider the atomic and electronic structures of  $Bi_2O_3$  nanocluster-modified TiO<sub>2</sub>. The nature of the valence band of  $Bi_2O_3$ -TiO<sub>2</sub>, with highlying  $Bi_2O_3$ -derived electronic states, permits the interaction of these Bi-O electronic states with the C and O atoms of  $CO_2$ . This can be considered similar to the case of the alkaline earth oxides, which show increased basicity and higher energy valence band states on going from Mg to Ca to Ba, and the interaction with  $CO_2$  is stronger with the increased basic character along this series.

**3.4. Hydrogenation of Adsorbed CO**<sub>2</sub>. Starting from the  $CO_2$  adsorption structures in Section 3.3, which show moderate adsorption energies and distortions to  $CO_2$  but no direct CO formation, we first examined the dissociation and formation of CO and adsorbed oxygen. However, such starting structures relax back to those already described, and if we remove CO, this is endothermic by up to 3 eV.

We have therefore examined the first steps in hydrogenation to explore if the adsorbed  $CO_2$  species can be hydrogenated. We focus on Bi<sub>4</sub>O<sub>6</sub>-rutile and Bi<sub>4</sub>O<sub>6</sub>-anatase, with the most favorable  $CO_2$  adsorption modes discussed above. We adsorb a hydrogen atom at the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructure to simulate the dissociation of H<sub>2</sub> and the formation of a hydroxyl on the nanocluster. We then use the climbing image NEB method with three images to determine the activation barrier for H migration, from which either a formate or carboxyl species can be produced.

Figure 8a,b shows the structure of the H atom adsorbed as a hydroxyl on  $Bi_4O_6$ -rutile and  $Bi_4O_6$ -anatase. The energy gain



**Figure 8.** (a) Atomic structure of a hydroxyl species on Bi<sub>4</sub>O<sub>6</sub>-rutile with adsorbed CO<sub>2</sub>. Hydrogen is denoted by the white sphere. (b) Atomic structure of a hydroxyl species on Bi<sub>40</sub>O<sub>6</sub>-anatase with adsorbed CO<sub>2</sub>. (c) Atomic structure of the transition state for H migration to adsorbed CO<sub>2</sub> on Bi<sub>4</sub>O<sub>6</sub>-rutile. (d) Atomic structure of the transition state for H migration to adsorbed CO<sub>2</sub> on Bi<sub>4</sub>O<sub>6</sub>-rutile. (e) Atomic structure of a COOH intermediate on Bi<sub>4</sub>O<sub>6</sub>-rutile. (f) Atomic structure of a COOH intermediate on Bi<sub>4</sub>O<sub>6</sub>-rutile.

relative to 1/2 H<sub>2</sub> (in gas phase) is 1.42 eV on Bi<sub>4</sub>O<sub>6</sub>-rutile and 0.63 eV on Bi<sub>4</sub>O<sub>6</sub>-anatase. These are moderate energy gains for hydrogen adsorption. Upon H adsorption at Bi<sub>4</sub>O<sub>6</sub>-rutile, the O-H distance is 0.98 Å, and the Bi-O distances involving this oxygen are 2.25 and 2.44 Å. On Bi<sub>4</sub>O<sub>6</sub>-anatase, the O-H distance is 1.01 Å, and the Bi-O distances for this oxygen are 2.31 and 2.18 Å.

The computed barrier for H migration from the hydroxyl to oxygen in  $CO_2$  to form a carboxyl intermediate is 0.77 eV on  $Bi_4O_6$ -rutile (110) and 0.68 eV on  $Bi_4O_6$ -anatase (101). These are moderate barriers for the H transfer to the adsorbed  $CO_2$ . The atomic structure of the transition state is shown in Figure 8c,d. In the transition state on  $Bi_4O_6$ -rutile, the H atom has migrated away from the nanocluster toward the oxygen of the adsorbed  $CO_2$ . On  $Bi_4O_6$ -anatase, the transition state involves the H atom migrating away from the oxygen of the nanocluster by 0.25 Å toward  $CO_2$ .

The atomic structure of the carboxyl intermediate on  $\text{Bi}_4\text{O}_6$ rutile and  $\text{Bi}_4\text{O}_6$ -anatase is shown in Figure 8e,f. For the COOH intermediates, the C=O, C-O(H), OH, and C-O(Bi) distances are presented in Table 4. We also examined the formation of a formate intermediate. However, formate either lies higher by ca. 3 eV, on  $\text{Bi}_4\text{O}_6$ -rutile, or is not stable, relaxing to COOH on  $\text{Bi}_4\text{O}_6$ -anatase, and thus the COOH intermediate is preferred. If we introduce a second hydrogen atom to make COOH<sub>2</sub>, this always relaxes to water and CO<sub>2</sub>, removing oxygen from the  $\text{Bi}_2\text{O}_3$  nanocluster, and thus we

Table 4. Computed C=O, C-O(H), OH, and C-O(Bi) Distances in COOH Intermediates on  $Bi_4O_6$ -Rutile and  $Bi_4O_6$ -Anatase in Å

Bi <sub>4</sub> O <sub>6</sub> -rutile (110)		Bi <sub>4</sub> O <sub>6</sub> -anatase (101)	
С=О	1.24	С=О	1.24
C-O(H)	1.35	C-O(H)	1.37
ОН	0.98	OH	0.98
C–O(Bi)	1.31	C–O(Bi)	1.31

conclude that although  $CO_2$  can adsorb at the oxidized  $Bi_2O_3$ -TiO<sub>2</sub> nanoclusters, it is difficult to hydrogenate to useful products.

## 4. CONCLUSIONS

We have studied the interaction and activation of  $CO_2$  at the novel heterostructure of  $Bi_2O_3$  nanoclusters supported on rutile and anatase  $TiO_2$  surfaces. Previous experimental work has demonstrated that Bi-containing materials can activate and convert  $CO_2$  to more useful molecules, but the origin of this is not yet clear.

The Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructures can be reduced, with moderate energy costs, which should be possible through a thermochemical process or by the addition of hydrogen. This results in the reduction of Ti sites, and Bi sites in the nanocluster can also be reduced. The interaction of the reduced heterostructures with CO<sub>2</sub> can result in direct exothermic CO formation, or charge transfer to CO<sub>2</sub> (reoxidizing Bi and Ti cations), to give an activated carboxylate species. The CO can be removed, and the addition of hydrogen is an exothermic process that forms water and reduces the nanocluster. This suggests a promising approach for CO<sub>2</sub> conversion via CO.

We find that  $CO_2$  adsorbs moderately strongly at the oxidized  $Bi_2O_3$ -TiO<sub>2</sub> heterostructures, with the computed adsorption energies ranging from -0.54 to 1.01 eV; van der Waals interactions simply shift these energies by ca. 0.15 eV, but do not change the overall trends.  $CO_2$  adsorbs in a carbonate-like adsorption mode (but is not overstabilized), with no charge transfer to the molecule. Finally, the computed vibrational modes of the adsorbed  $CO_2$  show a significant red shift of over 750 cm<sup>-1</sup> in the C=O stretching mode and a breaking of the degeneracy in the O-C-O bending mode. The magnitude of the red shift in the C=O stretching mode correlates with the strength of the adsorption of  $CO_2$ . The position of the high-lying valence band states derived from  $Bi^{3+}$ -O interactions appear to drive the activation of  $CO_2$ .

We find that the CO<sub>2</sub> adsorbed in this fashion can be hydrogenated to a COOH intermediate, with the migration barriers from the nanocluster to the adsorbed CO<sub>2</sub> of less than 0.8 eV, whereas CO<sub>2</sub> dissociation is not favorable. However, further hydrogenation of COOH does not result in any useful products, and we conclude that reduction is the key to the activation and subsequent conversion of CO<sub>2</sub> on Bi<sub>2</sub>O<sub>3</sub>modified TiO<sub>2</sub> heterostructures.

These results show that the unique properties of bismuthcontaining oxides can be exploited to adsorb and activate carbon dioxide, which is the key first step in the reductive conversion of  $CO_2$  to useful molecules. The combination of a non-bulk-like nanocluster-containing  $Bi^{3+}$  species, which is reducible, provides an interesting material that can activate  $CO_2$ , whether that be by strong adsorption and distortion, electron transfer to form a carboxylate, or by direct breaking of a C–O bond, and we propose that these heterostructures can be synthesized and tested for  $CO_2$  activation.

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#### Notes

The author declares no competing financial interest.

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