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# **Activation of CO<sub>2</sub> at Chromia-Nanocluster-Modified Rutile and Anatase**

**TiO<sub>2</sub>**

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## **Abstract**

Converting CO<sub>2</sub> to fuels is required to enable the production of sustainable fuels and to contribute to alleviating CO<sub>2</sub> emissions. In considering conversion of CO<sub>2</sub>, the initial step of adsorption and activation by the catalyst is crucial. In addressing this difficult problem, we have examined how nanoclusters of reducible metal oxides supported on TiO<sub>2</sub> can promote CO<sub>2</sub> activation. In this paper we present density functional theory (DFT) simulations of CO<sub>2</sub> activation on heterostructures composed of clean or hydroxylated extended rutile and anatase TiO<sub>2</sub> surfaces modified with chromia nanoclusters. The heterostructures show non-bulk Cr and O sites in the nanoclusters and an upshifted valence band edge that is dominated by Cr 3d- O 2p interactions. We show that the supported chromia nanoclusters can adsorb and activate CO<sub>2</sub> and that activation of CO<sub>2</sub> is promoted whether the TiO<sub>2</sub> support is oxidised or

hydroxylated. Reduced heterostructures, formed by removal of oxygen from the chromia nanocluster, also promote CO<sub>2</sub> activation. In the strong CO<sub>2</sub> adsorption modes, the molecule bends giving O-C-O angles of 127 - 132° and elongation of C-O distances up to 1.30 Å; no carbonates are formed. The electronic properties show a strong CO<sub>2</sub>-Cr-O interaction that drives the interaction of CO<sub>2</sub> with the nanocluster and induces the structural distortions. These results highlight that a metal oxide support modified with reducible metal oxide nanoclusters can activate CO<sub>2</sub>, thus helping to overcome difficulties associated with the difficult first step in CO<sub>2</sub> conversion.

**Keywords:** DFT; CO<sub>2</sub> activation; adsorption; heterostructures

## 1. Introduction

CO<sub>2</sub> emissions from fossil fuels are the major cause of climate change and need to be eliminated in the near future to meet the targets of the COP21 Paris agreement to keep average global temperature increases below 2°C. Thus finding solutions to remove and store or use this CO<sub>2</sub> is a key concern. A solar driven photo- or thermochemical process for the conversion of CO<sub>2</sub> to CO, coupled with solar water splitting can produce synthesis gas, while direct conversion of CO<sub>2</sub> to liquid fuels would enable a sustainable approach to producing fuels and storing solar energy in high energy chemical bonds[1-11].

However, CO<sub>2</sub>, as the most oxidised form of carbon, is highly stable and therefore activating it as part of the conversion process is difficult. In fact, to date, there are no widely available catalysts that can exploit solar energy (either directly or via thermochemical processes) to efficiently reduce CO<sub>2</sub> to useful chemicals. One successful example of a photocatalyst has been Pt-modified TiO<sub>2</sub> nanotubes[8, 12, 13] that produce methane. 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.

Copper has been shown to promote conversion of CO<sub>2</sub> into hydrocarbons, while many other metallic catalysts promote hydrogen evolution. More recently, catalysts based on oxide-derived Cu or Cu with mixed oxidation states have been shown to reduce CO<sub>2</sub> to useful molecules such as methane, methanol or ethanol [2, 14-26]. While this is encouraging, there is still an urgent need from a fundamental perspective to understand the factors that drive CO<sub>2</sub> activation and find materials to promote this process. Since a CO<sub>2</sub> anion (CO<sub>2</sub><sup>δ-</sup>) is implicated in CO<sub>2</sub> conversion, using materials with excess electrons is one path to the development of CO<sub>2</sub> activation catalysts. These electrons could be produced through light excitation or formation of oxygen vacancies which release electrons to the catalyst. Transition metal-oxide based catalysts could show some promise in this regard; the work on Cu-based catalysts suggests a pathway towards exploiting reducible metal oxides for CO<sub>2</sub> conversion. It is also possible to promote CO<sub>2</sub> activation without necessarily producing an anionic species and this would be driven by interactions at suitable sites in the catalyst and/or suitable energy level alignments of the catalyst and CO<sub>2</sub>.

Irrespective of the origin of the electrons that reduce CO<sub>2</sub>, in any CO<sub>2</sub> conversion process the initial adsorption and activation of CO<sub>2</sub> is a key step. Thereafter there may be transfer of electron(s) to the CO<sub>2</sub> through light absorption or from excess electrons present in the catalyst after catalyst (pre-)reduction or in a combined PV+electrolysis system. Thus, the key challenge in fuel production from CO<sub>2</sub> is to discover catalysts that will promote the crucial first step, namely the adsorption and activation of CO<sub>2</sub>.

Copper-based catalysts have been widely studied for CO<sub>2</sub> activation and conversion and this includes Cu metal, oxide-derived Cu and mixed oxidation state Cu [2, 14-26]. Modelling the

interaction of CO<sub>2</sub> with copper oxides uses density functional theory (DFT) to provide insights for further development of CO<sub>2</sub> activation catalysts. Wu *et al.* studied the adsorption of CO<sub>2</sub> at the Cu<sub>2</sub>O (111) surface with oxygen vacancies [17], and found that dissociative adsorption was thermodynamically unfeasible. In addition, while a CO<sub>2</sub><sup>δ-</sup> radical anion species can form on a defective surface, this is not stable. Wu *et al.* examined at the adsorption of CO<sub>2</sub> at Cu<sub>2</sub>O (111) using Hybrid DFT [21] and found adsorption only in non-activated form. This was confirmed by Bendavid and Carter [18]. Mishra *et al.* found similar results for CO<sub>2</sub> adsorption at Cu<sub>2</sub>O (111), but reported strong chemisorption at the high energy Cu-O terminated (110) surface[14] and at the (011) surface of CuO [2]. Uzunova *et al.* studied the conversion of CO<sub>2</sub> to methanol on Cu<sub>2</sub>O nanolayers and clusters [16] using Hybrid DFT. In the work of Favaro *et al.*[24] a model of Cu with subsurface oxygen was found to activate CO<sub>2</sub>.

The adsorption of CO<sub>2</sub> molecules at different titania surfaces, including rutile and anatase, and nanostructures has also been well studied and the role of low coordinated sites, surface structure and oxygen vacancies has been discussed [27-32]. The presence of excess electrons and holes was shown to drive adsorption and activation of CO<sub>2</sub> at rutile (110) [33]. Yang *et al.* showed that sub-nm Pt clusters at the anatase (101) surface enhanced CO<sub>2</sub> activation through providing of additional adsorption sites and the transfer of electron density to the TiO<sub>2</sub> substrate [34]. Fewer studies exist for other metal oxide systems, but some examples include Cu/CeO<sub>2</sub> and Cu/CeO<sub>2</sub>/TiO<sub>2</sub> [35], Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> [36] and dispersed CeO<sub>2</sub>/TiO<sub>2</sub> [37]; the role of Ce<sup>3+</sup> in visible light absorption, photogenerated charge separation and strengthening CO<sub>2</sub>-surface bonding was highlighted.

Previously we have used first principles density functional theory (DFT) simulations to study heterostructured materials composed of TiO<sub>2</sub> (rutile or anatase) modified with metal oxide nanoclusters. In earlier work, the emphasis focussed on systems with predicted visible light absorption[38-49] and reduced charge recombination[39-43, 50, 51]. We have begun to extend

this work to study the interaction of molecules, such as CO<sub>2</sub>, with these metal oxide nanocluster modified TiO<sub>2</sub> systems [38, 52]. We have investigated modified TiO<sub>2</sub> systems, *e.g.* ZrO<sub>2</sub>-anatase, where CO<sub>2</sub> can adsorb and be activated [38] and reduced MnO<sub>x</sub>-TiO<sub>2</sub> which show weak or unfavourable interactions with CO<sub>2</sub> [52]. There is therefore still much work to be done to understand the factors that drive CO<sub>2</sub> activation on metal oxides.

In the present paper, we use first principles density functional theory to examine in detail the interaction and activation of CO<sub>2</sub> at Cr<sub>2</sub>O<sub>3</sub> nanocluster modified rutile and anatase TiO<sub>2</sub> surfaces, which are oxidised or hydroxylated. The interaction of CO<sub>2</sub> with reduced Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructures, upon loss of oxygen from the nanocluster, is also examined. While chromia is by far less studied for CO<sub>2</sub> adsorption compared to other oxides, there have a number of experimental surface science studies devoted to this topic [53-57]. These have discussed difficulties in obtaining high quality films of chromia or single crystals of Cr metal. Thus, chromia grown through oxidation of metallic Cr or chromia micropowders have been employed. These studies use infra red (IR) spectroscopy and thermal desorption spectroscopy (TDS) to examine the role of the termination of the chromia film on CO<sub>2</sub> adsorption. Termination with Cr enables strong adsorption of CO<sub>2</sub>, as determined from TDS, with formation of carboxylate or carbonates. Termination with chromyl oxygen can bury these Cr sites and facilitates physisorption of linear CO<sub>2</sub>, with a lower temperature TDS peak. The IR spectra show clear differences between the CO<sub>2</sub> adsorption modes. We find that chromia modified TiO<sub>2</sub> heterostructures are able to activate CO<sub>2</sub>, causing O-C-O bending and elongation of C-O distances. This is independent of the state or identity of the TiO<sub>2</sub> surface, indicating that chromia nanoclusters drive CO<sub>2</sub> activation. In addition, reduced Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructures also activate CO<sub>2</sub>. These findings thus show that transition metal oxide nanocluster modification of rutile and anatase TiO<sub>2</sub> produces heterostructures that can activate CO<sub>2</sub>.

## 2. Methods

Following our approach from previous work on chromia-modified rutile and anatase[58] we prepare heterostructures of nanoclusters with Cr<sub>4</sub>O<sub>6</sub> stoichiometry supported on rutile (110) and anatase (101); the Supporting Information contains full details. We use a three dimensional periodic surface slab within VASP [59-62], and a plane wave basis set. Projector augmented wave potentials[63, 64], with 4, 12, 6, 4 and 1 valence electrons for Ti, Cr, O, C and H are used [58]. The cut-off for the kinetic energy is 396 eV and the exchange-correlation functional is the Perdew-Wang 91[65] approximation. A Monkhorst-Pack (2×1×1)  $\mathbf{k}$ -point sampling grid is used. We apply the DFT+U approach [66] to describe the Ti 3d and Cr 3d states, with U = 4.5 eV for the Ti 3d states and 3.5 eV for the Cr 3d states [67, 68]. This DFT+U set-up is designed to recover a consistent description of the localisation of electrons in reduced cations rather than to recover the band gap. Convergence criteria for electronic and ionic relaxations are 0.0001 eV and 0.02 eV/ Å. All calculations are spin polarised.

(2x4) and (4x2) surface supercell expansions are employed for rutile and anatase, respectively and the vacuum gap in all cases is 12 Å. The TiO<sub>2</sub> surfaces are unmodified oxidised or hydroxylated rutile (110) and anatase (101) surfaces [40, 58]. The free chromia nanoclusters are relaxed within the same computational described above, starting from different atomic arrangements. The most stable atomic structure of the free chromia Cr<sub>4</sub>O<sub>6</sub> nanocluster is then adsorbed on the oxidised and hydroxylated TiO<sub>2</sub> surfaces in different adsorption configurations and these are relaxed. We then use the most stable relaxed chromia-TiO<sub>2</sub> heterostructures for subsequent study with CO<sub>2</sub> [39, 48, 51]. When clean rutile is modified with Cr<sub>4</sub>O<sub>6</sub>, this is denoted **Cr<sub>4</sub>O<sub>6</sub>-o-rutile** and when hydroxylated rutile is modified with Cr<sub>4</sub>O<sub>6</sub>, this is denoted **Cr<sub>4</sub>O<sub>6</sub>-oh-rutile**; a similar nomenclature is used for anatase. The term **Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** indicates a

non-specific Cr<sub>2</sub>O<sub>3</sub> nanocluster-modified TiO<sub>2</sub> heterostructure. Although the detailed study of the interaction of water at chromia-TiO<sub>2</sub> heterostructures is beyond the scope of this work, we have found that adsorption of water at Cr<sub>4</sub>O<sub>6</sub>-o-rutile and Cr<sub>4</sub>O<sub>6</sub>-oh-rutile is molecular with adsorption energies of -0.3 and -0.8 eV, so that there is a barrier to hydroxyl formation on adsorbed chromia.

The stability of the heterostructure is characterised by the nanocluster adsorption energy, E<sup>ads</sup>

$$E^{ads} = E[(Cr_4O_6)-TiO_2] - \{E[(Cr_4O_6)] + E[TiO_2]\} \quad (1)$$

Where E[(Cr<sub>4</sub>O<sub>6</sub>)-TiO<sub>2</sub>] is the computed total energy of Cr<sub>4</sub>O<sub>6</sub> nanocluster-modified TiO<sub>2</sub>, E(Cr<sub>4</sub>O<sub>6</sub>) is the computed total energy of the free Cr<sub>4</sub>O<sub>6</sub> nanocluster and E(TiO<sub>2</sub>) is the computed total energy of the unmodified TiO<sub>2</sub> (rutile/anatase) surface.

The CO<sub>2</sub> adsorption energy is defined in Eqn (2):

$$E^{ads} = E[CO_2@Cr_4O_6-TiO_2] - \{E[Cr_4O_6-TiO_2] + E[CO_2]\} \quad (2)$$

where E[CO<sub>2</sub>@Cr<sub>4</sub>O<sub>6</sub>-TiO<sub>2</sub>] is the computed total energy of CO<sub>2</sub> adsorbed at Cr<sub>4</sub>O<sub>6</sub>-modified TiO<sub>2</sub>.

### 3. Results

We first briefly summarise the atomic structure of chromia-modified rutile and anatase TiO<sub>2</sub>, in which the TiO<sub>2</sub> supports are oxidised or hydroxylated ½ ML coverage. These are shown in **Figures S1 and S2** of the supporting information. Adsorption and relaxation of Cr<sub>4</sub>O<sub>6</sub> on both TiO<sub>2</sub> surfaces gives adsorption energies of -4.25 eV and -5.85 eV on oxidised rutile and anatase and -1.08 eV and -2.21 eV on hydroxylated rutile and anatase, indicating strong nanocluster-surface interactions. The presence of surface hydroxyls and the migration of hydrogen to the support nanocluster reduce the energy gain upon chromia adsorption at hydroxylated surfaces.

Ti and Cr sites have the expected +4 and +3 oxidation states. Exceptions to this are  $\text{Cr}_4\text{O}_6$ -o-anatase, where a reduced  $\text{Ti}^{3+}$  and an oxidised  $\text{Cr}^{4+}$  cation are formed, and  $\text{Cr}_4\text{O}_6$ -oh-anatase, where 2  $\text{Cr}^{2+}$  and 2  $\text{Cr}^{4+}$  cations are present. In all heterostructures, the valence band edge is modified by the adsorption of  $\text{Cr}_4\text{O}_6$  pushing the VB edge to higher energy. Oxygen vacancies can form readily in these systems, with formation energies of 0.22 eV and 1.95 eV on  $\text{Cr}_4\text{O}_6$ -o-rutile and  $\text{Cr}_4\text{O}_6$ -o-anatase, while these formation energies are 0.69 eV and 0.35 eV on  $\text{Cr}_4\text{O}_6$ -oh-rutile and  $\text{Cr}_4\text{O}_6$ -oh-anatase. Upon reduction, heterostructures of chromia on oxidised and hydroxylated supports show the presence of reduced  $\text{Ti}^{3+}$  and  $\text{Cr}^{2+}$  species.

### **3.1 Adsorption and Activation of CO<sub>2</sub> at Chromia-Modified Rutile (110) and Anatase (101)**

#### *3.1.1 CO<sub>2</sub> Adsorption at Cr<sub>4</sub>O<sub>6</sub>-modified rutile*

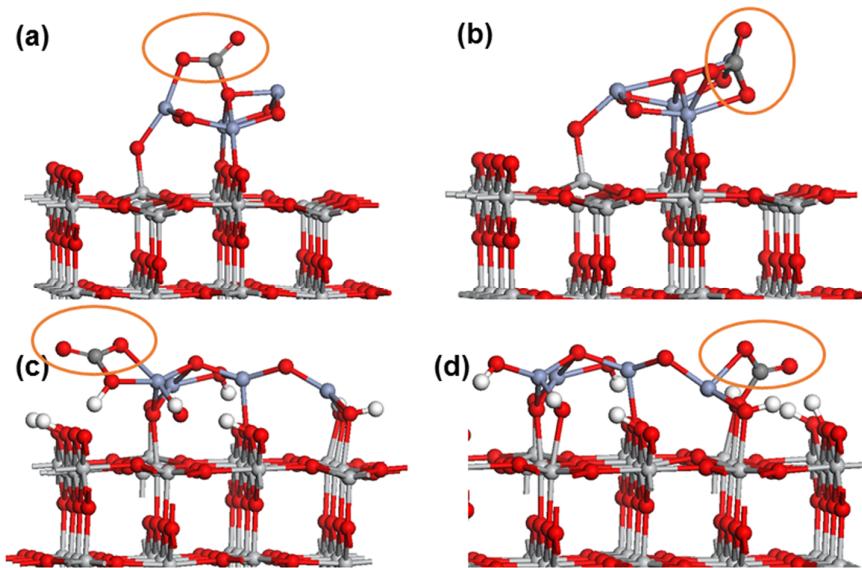
**Figure 1** shows the atomic structure for the two most stable CO<sub>2</sub> adsorption modes that we have found at  $\text{Cr}_4\text{O}_6$ -o-rutile (110) (Figure 1(a), (b)), modes I and II) and  $\text{Cr}_4\text{O}_6$ -oh-rutile (110) (Figure 1(c), (d) modes I and II). The computed adsorption energies for the two CO<sub>2</sub> adsorption modes on  $\text{Cr}_4\text{O}_6$ -o-rutile (110) are -0.63 eV and -0.91 eV for modes I and II. In  $\text{Cr}_4\text{O}_6$ -oh-rutile (110), the CO<sub>2</sub> adsorption energies are -0.92 eV and -0.31 eV for modes I and II. Clearly the modification of rutile with chromia produces heterostructures that show moderately strong adsorption capability for CO<sub>2</sub>, which is the first requirement for CO<sub>2</sub> conversion. These energies are 0 K DFT energy differences and if we include the zero point energy corrections (ZPE) for CO<sub>2</sub> adsorption these are only on the order of 0.03 eV which makes no significant change to the adsorption energies at chromia-modified TiO<sub>2</sub>. If we compare with the available

work on CO<sub>2</sub> adsorption at chromia, then the moderately strong adsorption energies can arise from the availability of Cr sites in the nanocluster to interact with oxygen of CO<sub>2</sub>, in a similar to the stronger Cr-CO<sub>2</sub> interaction described experimentally in refs[54-56].

We have examined multiple CO<sub>2</sub> adsorption sites on each chromia-TiO<sub>2</sub> system and other, less favourable adsorption modes are shown in Figures S3 and S4 and the energies relative to the most stable adsorption mode are shown in Table S1 of the Supporting Information. Even though these adsorption modes are less stable than those shown in Figure 1, we can see that they still generally show moderate CO<sub>2</sub> adsorption energies and similar adsorption structures, so that CO<sub>2</sub> adsorption and activation at multiple sites of chromia-modified TiO<sub>2</sub> is likely. We have also relaxed the adsorption structures in Figure 1 with no +U correction and find that the adsorption of CO<sub>2</sub> and the changes to its geometry are not influenced by the inclusion of the +U correction into the computational set-up.

In discussing the adsorption structure of CO<sub>2</sub>, we focus on the change in molecular C-O distances and the O-C-O angle. In gas phase CO<sub>2</sub>, the C-O distances are 1.16 Å, while the O-C-O angle is 180°. On Cr<sub>4</sub>O<sub>6</sub>-o-rutile, CO<sub>2</sub> adsorption in mode I results in the C-O distances elongating to 1.27 and 1.23 Å, while the O-C-O angle is 132°. One oxygen atom of CO<sub>2</sub> binds to a Cr site in the nanocluster, with a Cr-O distance of 2.05 Å. Finally, the C-O distance to the nanocluster is 1.44 Å. In adsorption mode II, the C-O distances in adsorbed CO<sub>2</sub> both lengthen to 1.27 Å and the O-C-O angle is 130°. Both oxygen atoms of the molecule bind to Cr sites in the nanocluster, with Cr-O distances of 2.08 Å and 2.13 Å. The carbon of CO<sub>2</sub> shows a C-O distance to the nanocluster of 1.39 Å. Thus, the adsorption of CO<sub>2</sub> causes a lengthening of molecular C-O distances and bending of the molecule, characteristic of CO<sub>2</sub> activation [4, 69]. We also note that the deviation from linearity in the O-C-O angle increases with the strength of CO<sub>2</sub> adsorption.

Finally, we have computed the vibrational frequencies of adsorbed CO<sub>2</sub>; for reference our computed vibrational modes for gas-phase CO<sub>2</sub> are 2354, 1325, and 632 cm<sup>-1</sup> and the experimental CO<sub>2</sub> vibrational modes are 2349, 1333 and 667 cm<sup>-1</sup> [70] so that our gas phase CO<sub>2</sub> vibrational modes are in good agreement with experiment. In mode I, the computed vibrational modes are 1720, 1221, 791 and 767 cm<sup>-1</sup>, while in mode II, the vibrational modes are 1589, 1226, 921 and 803 cm<sup>-1</sup>. We note the large red shift of up to 765 cm<sup>-1</sup> in the C=O stretching mode and the lifting of the degeneracy of the O-C-O bending mode upon adsorption of CO<sub>2</sub> on the chromia nanocluster. The C-O elongation is not as large in mode I so the shift in the C=O stretching mode is correspondingly smaller. These results strongly indicate that CO<sub>2</sub> adsorbs in an activated mode.



**Figure 1:** Relaxed atomic structures for CO<sub>2</sub> adsorbed in two adsorption modes at **(a), (b)** Cr<sub>4</sub>O<sub>6</sub>-o-rutile and **(c), (d)** Cr<sub>4</sub>O<sub>6</sub>-oh-rutile. The colour scheme is Ti: grey spheres, O: red spheres, Cr: blue spheres and C: grey spheres. The ring shows the CO<sub>2</sub> molecule.

If we turn to activation of CO<sub>2</sub> at the Cr<sub>4</sub>O<sub>6</sub>-oh-rutile (110) heterostructure, adsorption of CO<sub>2</sub> in mode I (Figure 1(c)) results in an elongation of the molecular C-O distances to 1.21 and 1.31 Å, while the O-C-O angle is bent, with an angle of 132°. The C-O distance to the nanocluster is 1.44 Å and the Cr-O distance to the molecule is 1.99 Å. In adsorption mode II (Figure 1(d)), the C-O distances are 1.24 and 1.30 Å, while the O-C-O angle is 128°. We note the stronger elongation of one C-O distance upon adsorption at Cr<sub>4</sub>O<sub>6</sub>-oh-rutile compared to adsorption at Cr<sub>4</sub>O<sub>6</sub>-o-rutile. The oxygen involved is bound to Cr in the nanocluster, so this extra interaction permits a lengthening of the C-O bond.

The computed vibrational modes are 1774, 1152, 899, 796 cm<sup>-1</sup> and 1658, 1206, 927 and 772 cm<sup>-1</sup> for modes I and II, respectively. These are similar to CO<sub>2</sub> adsorption at the Cr<sub>4</sub>O<sub>6</sub>-o-rutile heterostructure and the non-uniform elongation of the C-O distances results in a smaller red shift in the C=O stretching mode. Thus, the interaction of CO<sub>2</sub> at chromia-modified rutile results in strong adsorption and activation of the molecule and this is irrespective of the state of the support. The activation of CO<sub>2</sub> is accompanied by distortions to the molecule, namely C-O bond elongation and O-C-O bending.

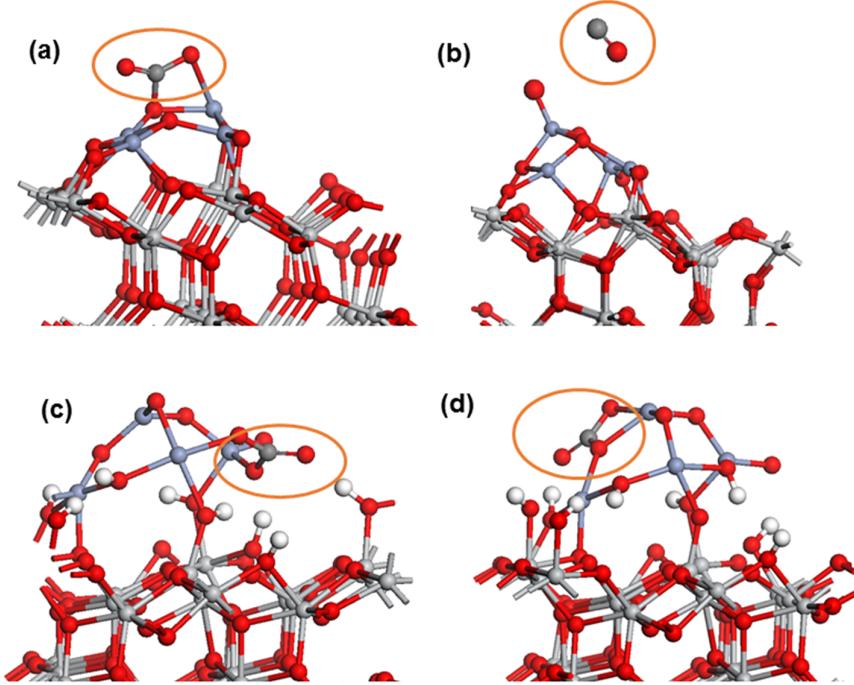
### 3.1.2 CO<sub>2</sub> Adsorption at Cr<sub>4</sub>O<sub>6</sub>-modified anatase

**Figure 2** shows the atomic structure for two CO<sub>2</sub> adsorption modes at Cr<sub>4</sub>O<sub>6</sub>-o-anatase (101) (Figure 2(a), (b)), modes I and II) and Cr<sub>4</sub>O<sub>6</sub>-oh-anatase (101) (Figure 2(c), (d) modes I and II). On Cr<sub>4</sub>O<sub>6</sub>-o-anatase (101), adsorption of CO<sub>2</sub> in mode I has a rather large adsorption energy of -2 eV, suggesting that the CO<sub>2</sub> may be overstabilised upon adsorption. In mode II, the computed adsorption energy is -0.13 eV. However, we note for adsorption mode II that a CO molecule is directly formed and this process is exothermic. The C-O distance in the free CO molecule is 1.14 Å.

In adsorption mode I, the C-O distances elongate to 1.26 and 1.28 Å and the O-C-O angle is 133°. The C-O distance to the nanocluster is 1.39 Å and the Cr-O distance to the molecule is 2.13 Å. Computed vibrational modes of adsorbed CO<sub>2</sub> in mode I are 1617, 1201, 915 and 906 cm<sup>-1</sup>, which again show activation of adsorbed CO<sub>2</sub>.

After CO<sub>2</sub> adsorption on Cr<sub>4</sub>O<sub>6</sub>-oh-anatase (101), the computed adsorption energies are -0.71 eV and -1.11 eV for modes I and II, respectively. In a similar fashion to the results on chromia-rutile, the availability of Cr sites in the nanocluster permits interaction with CO<sub>2</sub>. In mode I the molecular C-O distances are 1.25 and 1.28 Å, with an O-C-O bending angle of 127°. In mode II, the C-O distances are 1.24 and 1.29 Å and the O-C-O bending angle is 128°. Computed vibrational modes for adsorbed CO<sub>2</sub> are 1628, 1246, 908 and 799 cm<sup>-1</sup> on Cr<sub>4</sub>O<sub>6</sub>-o-anatase and 1642, 1243, 959 and 777 cm<sup>-1</sup> on Cr<sub>4</sub>O<sub>6</sub>-oh-anatase. Thus, the activation of CO<sub>2</sub> at chromia modified anatase is not dependence on the state of the TiO<sub>2</sub> support.

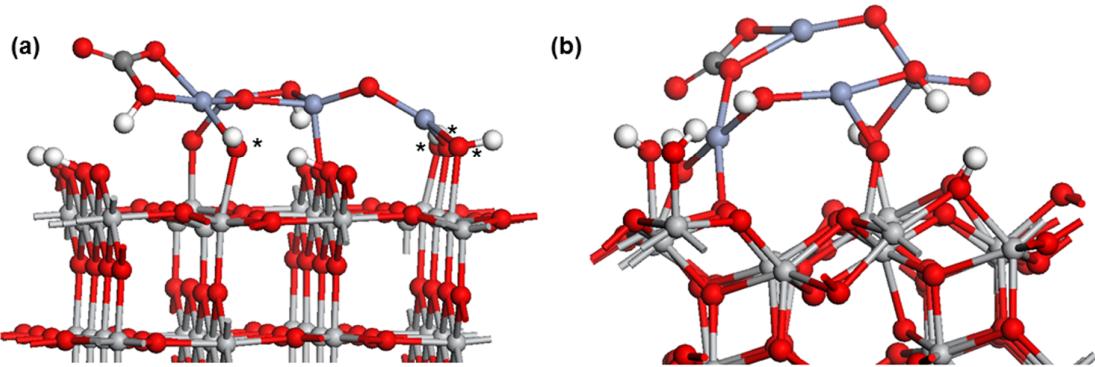
We recall that Cr<sub>4</sub>O<sub>6</sub>-o-anatase has a reduced Ti<sup>3+</sup> and a Cr<sup>4+</sup> cation [58]. Upon formation of activated CO<sub>2</sub> (mode I), both cations are partially reoxidised and there is a charge redistribution, with a transfer of 0.5 electrons to CO<sub>2</sub>. Upon formation of CO, examination of the computed indicates reoxidation of the Cr<sup>2+</sup> and Ti<sup>3+</sup>, with a transfer of 2 electrons to adsorbed CO<sub>2</sub> which promotes the formation of CO.



**Figure 2:** Relaxed atomic structures for CO<sub>2</sub> adsorbed in two adsorption modes at **(a), (b)** Cr<sub>4</sub>O<sub>6</sub>-o-anatase and **(c), (d)** Cr<sub>4</sub>O<sub>6</sub>-oh-anatase. The colour scheme is the same as Figure 1. The ring shows the CO<sub>2</sub> molecule.

### 3.2 Adsorption and Activation of CO<sub>2</sub> at Reduced Chromia-Modified Rutile and Anatase

We finally consider the adsorption of CO<sub>2</sub> at two examples of reduced Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, where the rutile and anatase supports are hydroxylated. Since in any process for conversion of CO<sub>2</sub>, water is likely to be used as a proton source, the supports will most likely have some coverage of water present and this is accounted for by using our ½ ML hydroxylated supports. In addition, the reduction energies of chromia-modified hydroxylated TiO<sub>2</sub> are moderate, so this needs to be taken into account when investigating CO<sub>2</sub> activation.



**Figure 3:** Relaxed atomic structures for CO<sub>2</sub> adsorbed at (a) reduced Cr<sub>4</sub>O<sub>5</sub>-oh-rutile and (b) reduced Cr<sub>4</sub>O<sub>5</sub>-oh-anatase. The colour scheme is the same as Figure 1.

**Figure 3** shows the atomic structure of CO<sub>2</sub> adsorbed at reduced Cr<sub>4</sub>O<sub>5</sub>-oh-rutile (110) and Cr<sub>4</sub>O<sub>5</sub>-oh-anatase (101). The computed CO<sub>2</sub> adsorption energies are -0.6 eV and -1.85 eV on rutile and anatase, respectively. The presence of the oxygen vacancy in the chromia nanocluster promotes adsorption of CO<sub>2</sub>, particularly on the anatase support. Hydrogen atoms from the hydroxyl sites do not migrate to the adsorbed CO<sub>2</sub>.

The C-O distances in the molecule elongate to 1.21 and 1.29 Å upon adsorption at Cr<sub>4</sub>O<sub>5</sub>-oh-rutile and to 1.24 and 1.31 Å upon adsorption at Cr<sub>4</sub>O<sub>5</sub>-oh-anatase. The corresponding O-C-O angles are 133° (rutile) and 127° (anatase). The third C-O distance to the nanocluster is 1.47 and 1.37 Å in Cr<sub>4</sub>O<sub>5</sub>-oh-rutile and Cr<sub>4</sub>O<sub>5</sub>-oh-anatase.

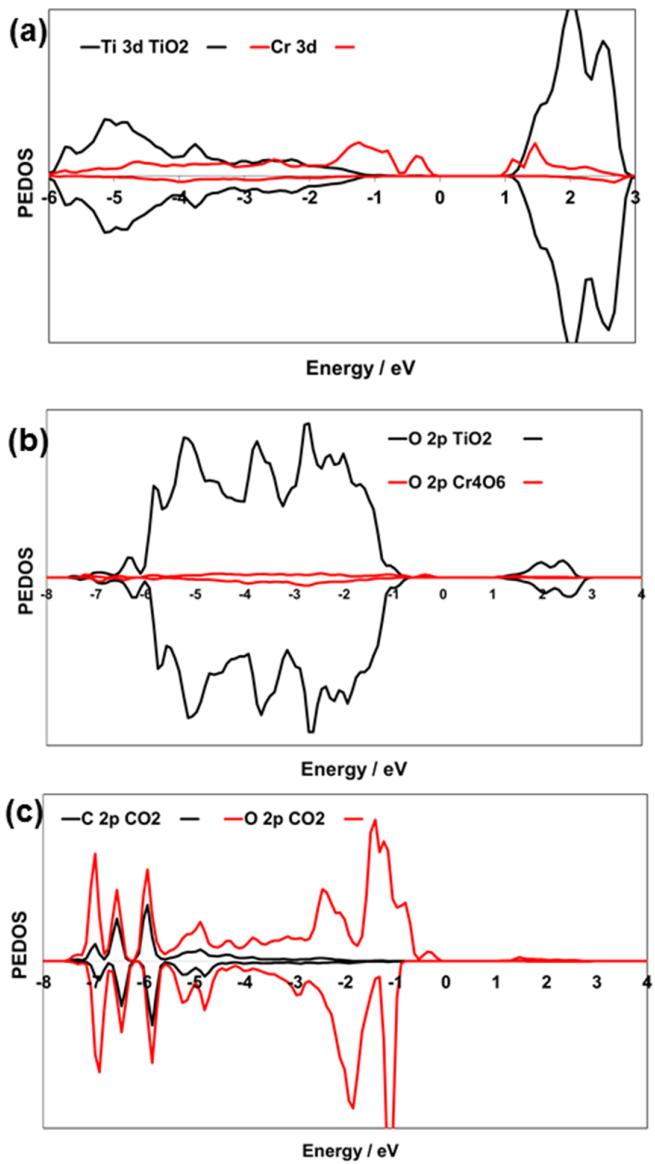
When we examine the oxidation states of the Ti and Cr cations in the supports and the nanocluster, the adsorption of CO<sub>2</sub> does not result in any significant change in the oxidation states of Ti and Cr cations; such changes are on the order of < 0.1 electrons so that reduced cation species persist. Thus, we suggest that there is some charge redistribution upon bonding with CO<sub>2</sub>.

#### **4. Discussion and Conclusion**

Finding materials that can activate CO<sub>2</sub> is of high interest for using CO<sub>2</sub> as a feedstock for sustainable fuel production. The present study shows that CO<sub>2</sub> can adsorb and activate at chromia nanocluster modified rutile and anatase TiO<sub>2</sub> heterostructures. We characterise the activation of CO<sub>2</sub> by the strength of adsorption, the elongation of C-O distances, the bending of the O-C-O angle and the red shift in the C=O stretching mode. In almost all cases we find moderately strong CO<sub>2</sub> adsorption; the exception is at Cr<sub>4</sub>O<sub>6</sub>-o-anatase. The C-O distances elongate, with a particularly strong elongation on chromia-anatase heterostructures, where the C-O distances elongate up to 1.30 Å. On chromia-rutile, the elongation is not uniform, with one C-O bond clearly longer than the other. The O-C-O angle always shows significant bending, where we find angles in the range of 127 – 132°. The state of the TiO<sub>2</sub> support, whether perfect or hydroxylated, and reduction of the chromia nanocluster, do not influence the adsorption and activation of CO<sub>2</sub> and it is therefore the chromia nanocluster modifier that promotes CO<sub>2</sub> adsorption.

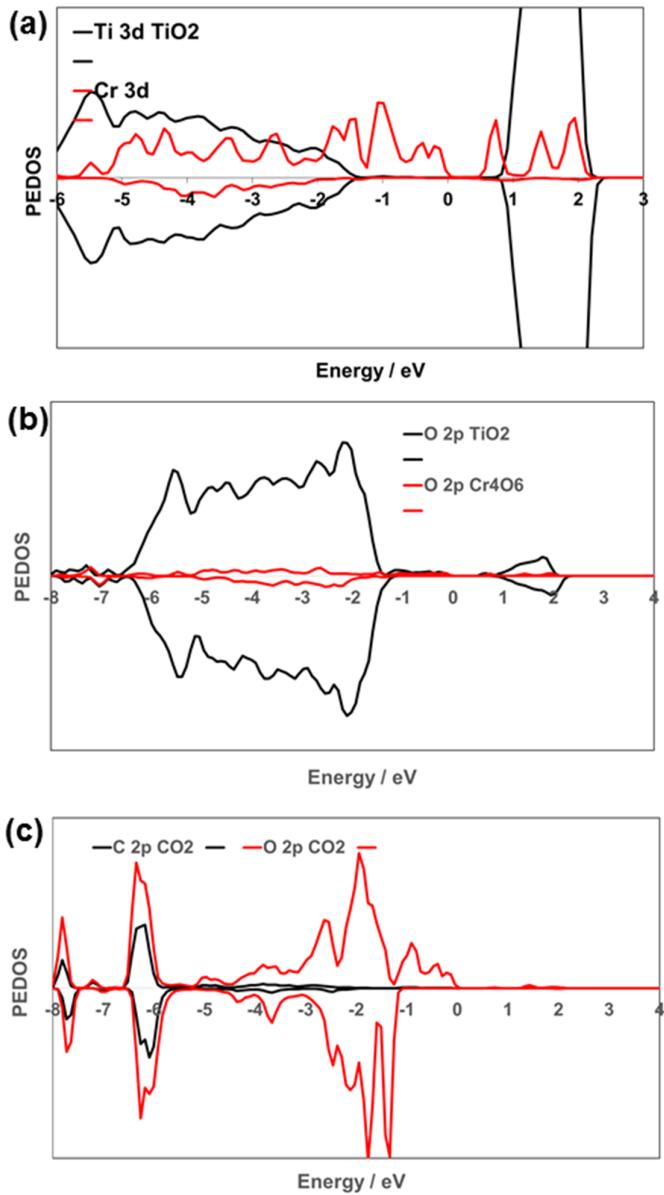
The supported nanoclusters offer some advantageous properties for CO<sub>2</sub> activation. Firstly, there are low coordinated metal and oxygen sites in such non-bulk like structures, which have the potential to be active towards molecular adsorption. Secondly the presence of non-bulk like atomic environments can modify the electronic structure relative to bulk materials and the support. To examine any electronic structure effects, we show the projected electronic density of states (PEDOS) for the examples of CO<sub>2</sub> adsorption in mode I on C<sub>4</sub>O<sub>6</sub>-oh-rutile and in mode I on Cr<sub>4</sub>O<sub>6</sub>-oh-anatase in Figures 4 and 5. We recall that in the heterostructures, there are Cr<sub>4</sub>O<sub>6</sub>-derived electronic states above the valence band edge of the TiO<sub>2</sub> support. The PEDOS show

that these states persist upon adsorption of CO<sub>2</sub>. Importantly, the CO<sub>2</sub> PEDOS, decomposed into C 2p and O 2p contributions, shows broad PEDOS peaks which are indicative of strong interactions between CO<sub>2</sub> and the oxide nanocluster. In particular, the O 2p states are found in the same energy range as the Cr<sub>4</sub>O<sub>6</sub> states, while the C 2p PEDOS is also broad in the region from -2 eV to -6 eV below the highest occupied states. Thus, it is clear that the position of the Cr<sub>4</sub>O<sub>6</sub>-TiO<sub>2</sub> electronic states is suitable to allow hybridisation with the C 2p and O 2p states of CO<sub>2</sub>. We note also that some supported chromia nanoclusters have Cr<sup>2+</sup> oxidation states, and reducing the heterostructure through oxygen removal produces Ti<sup>3+</sup> and Cr<sup>2+</sup> sites. After adsorption of CO<sub>2</sub>, we find that there can be reoxidation of these reduced cations, particularly in the case of CO formation, in which electron transfer from reduced Ti and Cr species is found. In other cases there is a redistribution of charge upon CO<sub>2</sub> adsorption. Thus, the chromia-modified TiO<sub>2</sub> heterostructures display suitable characteristics, namely active sites, suitable energy level positions and variable cation oxidation states which promote the adsorption and activation of CO<sub>2</sub>.



**Figure 4:** Projected electronic density of states for  $\text{CO}_2$  adsorbed on  $\text{Cr}_4\text{O}_6$ -oh-rutile (110).

The PEDOS is shown for Cr 3d and O 2p states in chromia, Ti 3d and O 2p states in  $\text{TiO}_2$  and C and O 2p states in adsorbed  $\text{CO}_2$ . The zero of energy is the top of the highest occupied states.



**Figure 5:** Projected electronic density of states for CO<sub>2</sub> adsorbed on Cr<sub>4</sub>O<sub>6</sub>-oh-anatase (110).

The PEDOS is shown for Cr 3d and O 2p states in chromia, Ti 3d and O 2p states in TiO<sub>2</sub> and C and O 2p states in adsorbed CO<sub>2</sub>. The zero of energy is the top of the highest occupied states.

In conclusion, the results of DFT studies of CO<sub>2</sub> adsorption at chromia-modified rutile and anatase TiO<sub>2</sub> surfaces show that these heterostructures are able to adsorb and activate CO<sub>2</sub>, thus contributing to expanding the range of oxide-based structures that can promote the critical first step in the conversion of CO<sub>2</sub>.

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