Exploring the Catalytic Properties of Unsupported and TiO₂-Supported Cu₅ Clusters: CO₂ Decomposition to CO and CO₂ Photoactivation

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ABSTRACT: In this work, we explore the decomposition of CO₂ on unsupported and TiO₂-supported Cu₅ clusters via computational modeling, using both finite cluster and periodic slab structures of the rutile TiO₂(110) surface. While the energy needed for C=O bond breaking is already significantly reduced upon adsorption onto the unsupported metal catalyst (it drops from 7.8 to 1.3 eV), gas desorption before bond activation is still the inevitable outcome due to the remaining barrier height even at 0 K. However, when the Cu₅ cluster itself is supported on TiO₂, reactant and product adsorption is strongly enhanced, the barrier for bond breaking is further reduced, and a spontaneous decomosition of the molecule is predicted. This finding is linked to our previous work on charge-transfer processes in the Cu₅−TiO₂ system triggered by solar photons, since a combination of both phenomena at suitable temperatures would allow for a photoinduced activation of CO₂ by sunlight.

1. INTRODUCTION

During the past few years, highly stable metal clusters of subnanometer size, as required in industrial applications, have emerged as a new generation of catalysts and photocatalysts with appealing properties arising from their molecule-like electronic structures. As opposed to metal nanoparticles in the visible region, these "atomic" or subnanometer-sized clusters do not sustain a metallic state and do not show plasmonic behavior. Instead, the presence of a molecule-like HOMO−LUMO gap impacts their chemical and physical properties, making them innovative materials for applications including luminescence, sensing, energy conversion, catalysis, and electrochemical applications. In particular, Cu₅ clusters have been shown to be less susceptible to oxidation than larger systems like Cu₆ or Cu₁₉ and have therefore been proposed as promising catalysts. Moreover, it has been observed that Cu₅ clusters are stable against oxidation up to a temperature as high as 423 K. These clusters can be synthesized by kinetic control using electrochemical methods, showing an exceptional chemical and thermodinamical stability in solution over the whole pH range. As discussed in ref 10, high monodispersity of synthesized Cu₅ clusters has been shown since the method of cluster synthesis was extremely size-selective. As compared with closed-shell cases, the outer unpaired electrons of open-shell clusters such as the Cu₅ cluster are expected to be more active in chemical reactivity either by sharing or transferring them. For all these reasons, we have chosen the Cu₅ as the potential catalysts in this work.

This article addresses the decomposition of CO₂ over Cu₅ into CO due to its potential relevance in the context of climate change and global warming (see ref 12 for a very recent and comprehensive review on heterogeneous CO₂ reduction). The CO₂ transformation onto copper clusters into methanol has recently attracted much attention. A deterrent in the CO₂ elimination is the high stability of the C=O bond, which necessitates an energy as high as 7.8 eV in order for it to be broken in the gas phase. The catalytic properties of metal clusters can be optimized through suitable supporting materials, which affect their geometry and electronic structure as desired. For instance, the electronic structure of Au₈ clusters is strongly influenced by the MgO support which increases its CO oxidation reactivity. For Cu₄ clusters, it could be shown that the Al₂O₃ support is lowering the energetic barrier for C=O bond-breaking to less than 1 eV due to the strong interaction of the CO₂ molecule with the copper cluster. Hence, similar effects are expected for a metal-oxide support of Cu₅ clusters.

In this work, the TiO₂ surface has been selected as the support due to its abundance, nontoxicity, biological inertness, and Mar...
and chemical stability. In fact, it is one of the most popular materials for (photo)catalytic applications and solar energy conversion. Moreover, we have recently shown that the deposition of a single monolayer of Cu4 clusters on a TiO2 surface improves its optical properties significantly,21 making it a visible-light photoactive material. More specifically, we demonstrate that, when deposited on the surface of titanium dioxide, the copper clusters are able to shift the adsorption from the high energy range, i.e. the UV spectrum, toward the visible light, where the sun has its maximum energy output. As a consequence, much more energy can be harvested from sunlight, and the coated titanium dioxide stores this energy temporarily in the form of charge pairs—electrons and holes—which is a perfect prerequisite for follow-up chemistry.

The CO2 activation and dissociation on TiO2-supported Cu4 (n ≤ 5)20 and Cu5 clusters21 has been addressed in previous works20,21 with the specific surface being rutile TiO2(110) in ref 20 and anatase TiO2(101) in ref 21. Thus, Iyempeurumal and Deskins20 found that clusters of 1–4 copper atoms supported on the rutile TiO2(110) surface stabilize a bent CO2 molecule (i.e., the precursors for CO2 decomposition), especially the Cu2 dimer. More recently, Jafarzadeh et al.21 considered, besides the CO2 activation, its dissociation into CO and O fragments attached to Cu4- and Ni1-modified anatase TiO2 surfaces, addressing also the impact of plasma-induced surface charging. The authors found that adding plasma-induced excess electrons stabilize further bent CO2 structures.21 Moreover, it was found that the dissociation of CO2 on charged clusters is energetically more favorable than that on neutral clusters.21 However, actual reaction paths to CO2 dissociation were not considered.

Applying density functional theory (DFT), time-dependent DFT, and an approach combining DFT with reduced density matrix theory, we focus on exploring the following aspects: (1) possible reaction energy pathways to both CO2 activation and dissociation on unsupported as well as TiO2-supported Cu4 clusters; (2) the optical response of the system under solar irradiation. Thus, in section 2, the computational approach and the details of our calculations are presented. Section 3 focuses on analyzing the reaction energy pathways as well as the UV–vis absorption spectra of unsupported and supported Cu5 clusters. Finally, section 4 closes with the concluding remarks.

2. METHODS

Density functional theory (DFT) is applied to shed light on the catalytic mechanism for CO2 decomposition to CO on unsupported and TiO2-supported Cu4 clusters. We employ a dispersion-corrected DFT-D3 ansatz22,23 given its excellent performance in describing the adsorption of small silver clusters on the same surface.24 Structural optimizations and the calculation of interaction energies are performed with the Perdew–Burke–Ernzerhof (PBE) density functional and the Becke–Johnson (BJ) damping22 for the D3 dispersion correction. We will refer to this combination as the PBE-D3(BJ) scheme. Both finite cluster and periodic slab models (see Figure 1) have been used to account for TiO2(110) rutile surface effects. We first explore minimum energy pathways for both physisorption and chemisorption of the CO2 molecule on supported and unsupported Cu4 clusters. Next, we seek for possible reaction pathways leading to C==O bond breaking, starting with the lowest-energy chemisorption states found for the attached CO2 molecule. Additionally, time-dependent density functional calculations of the UV–vis spectra are carried out to explore the possibility that a photoinduced activation of physisorbed CO2 occurs via electron transfer from TiO2-supported Cu4 clusters to the attached CO2 molecule. Finally, as a second route to obtain the UV–vis spectra, a reduced density matrix (RDM) approach in the Redfield approximation25 is employed, with the orbitals generated from periodic DFT calculations. In particular, we employed the HES06 hybrid functional of Heyd, Scuseria, and Ernzerhof,26,27 a well-established treatment for the band gap analysis of semiconductors including TiO2.28 This combined RDM-DFT treatment29,30 has provided UV–vis absorption spectra in very good agreement with the experiment for the Cu5-decorated rutile TiO2(110) surface.29

If not explicitly mentioned otherwise, distances and energies are given in angstrom (1 Å = 10−10 m) and electronvolt (1 eV = 1.60217665(35) × 10−19 m2 kg s−2) units, respectively.

2.1. Cluster Model Calculations. Cluster model calculations were performed by applying the PBE-D3(BJ) scheme
with the ORCA\textsuperscript{31} suite of programs (version 4.0.1.2). For this purpose, an atom-centered de\textit{f}2-TZVPP\textsuperscript{32} basis set was used for copper and carbon atoms while the (augmented) polarized correlation-consistent triple-\textit{ζ} (aug-cc-pVTZ) basis of Woon and Dunning, Jr.,\textsuperscript{33} as reported in ref 34, was employed for oxygen and titanium atoms. As can be seen from Figure 1 (left-hand panel), a hydrogen-saturated cluster model of stoichiometry (TiO\textsubscript{2})\textsubscript{13}(H\textsubscript{2}O)\textsubscript{14} was employed to model the rutile TiO\textsubscript{2}(110) surface, in which the number of hydrogen atoms are chosen so that the whole cluster remains electrically neutral. As mentioned in ref 19, this cluster model provides a very similar description of the Cu\textsubscript{5}−TiO\textsubscript{2}(110) system to that obtained via periodic calculations. For the sake of accuracy, we have also realized state-of-the-art periodic model calculations in this work (see section 2.2). In fact, the periodic model provides a better account of the extended nature of the surface and, particularly, of (long-range) dispersion corrections. However, the cluster model has allowed a vis-a-vis comparison of CO\textsubscript{2} adsorption properties on supported and unsupported Cu\textsubscript{5} clusters, as well as the application of more expensive ab \textit{initio} methods.

We assume the system to be in a doublet spin state since the quartet spin state is higher in energy for the free Cu\textsubscript{5} cluster (by 0.64 eV at PBE-D3(BJ) level). PBE-D3(BJ) interaction energies were found to agree within 10\% with reference values obtained with the domain-based pair natural orbital correlation approach DLPNO−CCSD(T)\textsuperscript{35} as well as the symmetry-adapted perturbation theory [SAPT(DFT)] method\textsuperscript{36,37} (see ref 24) for the related Ag\textsubscript{5}/TiO\textsubscript{2} system (see section 2.2.2). In fact, the periodic model provides a better account of the extended nature of the surface and, particularly, of (long-range) dispersion corrections.

When optimizing the geometries in the cluster model, the atoms of both CO\textsubscript{2} and Cu\textsubscript{5} subsystems were allowed to relax, while the atoms of the support were kept fixed to experimentally determined values of the TiO\textsubscript{2}(110)-(1×1) surface.\textsuperscript{38} Using this computational protocol, the adsorption energies were found to agree rather well with those obtained using the periodic slab model (see below), in which all the atoms were allowed to relax. Moreover, the employment of the ORCA suite of programs allowed us to obtain relaxed surface scans in constrained optimizations for which specific internal coordinates are kept frozen (i.e., the value of the C−O bond length). The modeling through a finite cluster was also used to test the performance of the PBE-D3(BJ) approach against higher levels of ab \textit{initio} theory such as second-order Möller−Plesset perturbation theory (MP2) level. This way, additional calculations on the physisorption interaction energies of CO\textsubscript{2} on TiO\textsubscript{2}-supported Cu\textsubscript{5} clusters showed that the PBE-D3(BJ) approach provides values agreeing to within 10\% with those obtained at MP2 level with the same basis set, and within 4\% with those calculated using the larger de\textit{f}2-QZVPP\textsuperscript{32} basis set and the same PBE-D3(BJ) scheme.

Time-dependent DFT (TDDFT) calculations of the UV−vis spectra were also performed using the PBE-D3(BJ) scheme and the cluster model. The number of roots were limited to 110 for the TiO\textsubscript{2}-supported Cu\textsubscript{5} cluster, with a focus on the first transition involving the “jump” of an electron from the highest-energy “doubled-occupied” molecular orbital (referred to as HOMO) of the complete system to an unoccupied molecular orbital with high density around the attached CO\textsubscript{2} molecule.

2.2. Periodic Calculations. Periodic electronic structure calculations are performed with the Vienna \textit{ab initio} simulation package (VASP 5.4.4)\textsuperscript{39,40} following a similar computational approach to that reported in previous work on He\textsubscript{−}, Ag\textsubscript{5}\textsuperscript{−}, and Cu\textsubscript{5}−TiO\textsubscript{2}(110) interactions\textsuperscript{19,24,41} as well as a systematic analysis of noble-gas atoms on the same surface.\textsuperscript{42} Electron−ion interactions are described by the projector augmented-wave method\textsuperscript{43,44} using PAW−PBE pseudopotentials as implemented in the program. The electrons of the O(2s, 2p), C(2s, 2p), Ti(3s, 4s, 3p, 3d) and Cu(3d, 4s) orbitals are treated explicitly as valence electrons. A plane wave basis set with a kinetic energy cutoff of 700 eV is used. A Gaussian smearing of 0.05 eV is employed to account for partial occupancies, and the Brillouin zone is sampled at the Γ point. Test calculations showed that interaction energies at the potential minimum, using a 5×5×1 Monkhorst−Pack\textsuperscript{44} k-point mesh, are similar (within ca. 0.01 eV) to those calculated at the Γ point. By shifting the kinetic energy cutoff from 700 to 1000 eV, the interaction energies were found to vary by less than 1 meV. The convergence criterion was 10\textsuperscript{−4} eV for the self-consistent electronic minimization. Geometries were relaxed with a force threshold of 0.02 eV/Å.

The Cu\textsubscript{5}-decorated surface was modeled via periodic slabs, using a 4×2 supercell (four TiO\textsubscript{2} trilayers giving ca. 13 Å slab width). Adsorption was modeled on one side of the slab, with 38 Å of vacuum above it. This large vacuum region allowed the description of long-range tails of the interaction potentials while avoiding unphysical overlaps of electronic densities. Interaction energies are derived via

\[
E_{\text{int}} = E_{\text{CO}_2/Cu_5} - E_{\text{Cu}_5} - E_{\text{CO}_2/TiO_2(110)}
\]

with \(E_{\text{Cu}_5/Cu_5/TiO_2(110)}\) as the total energy of the system, \(E_{\text{Cu}_5/TiO_2(110)}\) as the energy of the supported-TiO\textsubscript{2} Cu\textsubscript{5} cluster, and \(E_{\text{CO}_2}\) denoting the energy of the free (gas-phase) CO\textsubscript{2} molecule, all calculated in the same supercell slab for the sake of consistency.

Adsorption energies are calculated with the PBE-D3(BJ) scheme with the Hubbard term (DFT+U) added and including spin-polarization. The values of U reported in previous studies of Cu\textsubscript{5} clusters (\(U \leq S\)) on the (101) and (100) surfaces of anatase\textsuperscript{45} and rutile\textsuperscript{19} were used (4.2 eV for titanium and 5.2 eV for copper). Due to the known underestimation of the band gap with the PBE functional, the photoabsorption spectra are calculated with the HSE06 exchange-correlation functional instead, which uses a screened Coulomb potential for increased efficiency on metallic systems.\textsuperscript{36,37} This approach was applied using an HF/GGA mixing ratio of 25:75 with the screening parameter of 0.11 bohr\textsuperscript{−1} as recommended in ref 27. All the surface ions and atoms from both the Cu\textsubscript{5} cluster and the attached CO\textsubscript{2} molecule were relaxed using the PBE-D3(BJ) method but with the Hubbard term (DFT+U) added. Finally, the optimized geometries, obtained at the PBE+U/D3 level, were used in final HSE06 calculations of the electronic structures. This computational protocol is the same as in our previous calculations of the UV−vis spectra for the Cu\textsubscript{5}−TiO\textsubscript{2}(110) system.\textsuperscript{19}

2.2.1. Reduced Density Matrix Treatment. Photoabsorption spectra are calculated using the computational approach previously applied to the Ag\textsubscript{5}/TiO\textsubscript{2} and Cu\textsubscript{5}/TiO\textsubscript{2} systems in refs 19 and 24. The relaxation processes involved are described by the reduced density matrix (RDM) approach in the Redfield approximation,\textsuperscript{45} based on orbitals taken from calculations employing the HSE06 hybrid functional. This combination of RDM and DFT, proposed by Micha and
collaborators,\textsuperscript{29,30} has been successfully applied to silver\textsuperscript{24,46–48} and copper\textsuperscript{19} clusters on semiconductor surfaces.\textsuperscript{49}

Very briefly, in the presence of a monochromatic electromagnetic field $\mathcal{E}$ of frequency $\Omega$, the evolution equation for the reduced density $\rho$ in the Schrödinger picture takes the form

$$\dot{\rho}_{jk} = -\frac{i}{\hbar} \sum_l (F_{jl} \rho_{lk} - \rho_{jk} F_{lk}) + \sum_{l,m} R_{jklm} \rho_{lm}$$

with $\hat{F}^\text{KS}$ denoting the effective Kohn–Sham Hamiltonian (the indices refer to its representation in the Kohn–Sham basis set), $\mathcal{D}$ as the electric dipole moment operator, and $R_{jklm}$ as the Redfield coefficients, i.e., the Kohn–Sham components of the relaxation tensor. The latter are defined as in ref \textsuperscript{25} and are implemented as described in ref \textsuperscript{29}.

Figure 2. Surface scans characterizing the CO$_2$/Cu$_5$ interaction. Left-hand upper panel: relaxed surface scan (RSS) as a function of the distance between the carbon atom and the central atom of the (planar trapezoidal) Cu$_5$ cluster. Middle panel: RSS as a function of one C=O distance for the (planar trapezoidal) Cu$_5$ cluster. Bottom panel: RSS as a function of one C=O distance for the (bipyramidal) Cu$_5$ cluster. Right-hand panels: Gibbs energies as a function of temperature at the energy minimum (blue and red lines) and transition state (green lines) configurations as well as the asymptote for CO desorption from the Cu$_5$–O product species (dotted orange line). The nonperiodic cluster model has been used.
Within the Redfield approximation, the relaxation tensor incorporates not only fast electronic dissipation due to electronic fluctuations in the medium but also the relatively slow relaxation due to vibrations of the atomic lattice. It is convenient to perform a coordinate transformation into a rotating frame accounting for the electromagnetic field oscillation. This is described by the equations
\[ \tilde{\rho}_j(t) = \rho_j(t) \exp(i\Omega t), \quad \epsilon_i > \epsilon_j \]
\[ \tilde{\rho}_j(t) = \rho_j(t) \exp(-i\Omega t), \quad \epsilon_i < \epsilon_j \]
\[ \tilde{\rho}_j(t) = \rho_j(t) \]
where \( \epsilon_i \) is the energy of the ith Kohn–Sham orbital. Time averaging over the fast terms in the equation of motion for the RDM yields
\[ \tilde{\rho}^{SS}_j = \Gamma_j^{-1} \sum_{k=0}^{\infty} \Omega_k g_k(\Omega), \quad j \geq \text{HOMO} \]
\[ \tilde{\rho}^{SS}_j = 1 - \Gamma_j^{-1} \sum_{k=\text{LUMO}}^{\infty} g_k(\Omega), \quad j \leq \text{HOMO} \]
as stationary-state solutions for the diagonal elements.\(^{29}\) In it, HOMO and LUMO denote the lowest-energy unoccupied and the highest-energy occupied molecular orbital, respectively. \( \Gamma_j \) is a depopulation rate, and the sum terms \( g_k \) are given by
\[ g_k(\Omega) = \frac{\gamma \Omega_k}{\gamma^2 + \Delta_k^2(\Omega)^2} \]
with \( \gamma \) denoting the decoherence rate, \( \Omega_k \) as the Rabi frequencies given by \( \Omega_k = -D_k \epsilon_0/\hbar \) and \( \Delta_k(\Omega) = \Omega - (\epsilon_j - \epsilon_k) \) as detunings. The diagonal elements of the KS orbitals. The population relaxation rate \( \hbar \Gamma \) and the decoherence rate \( \hbar \gamma \) are kept fixed to values of 0.15 and 150 meV (27 ps and 27 fs). These values have been chosen according to known rates for phonon decay and electronic density excitations in semiconductors (see, e.g., ref 50).

In terms of the stationary populations, the absorbance is given by\(^{18,24,47,48,51}\)
\[ \alpha(\Omega) = \sum_{j=\text{HOMO}}^{\text{LUMO}} \sum_{k=\text{LUMO}}^{\infty} \bar{f}_{jk} (\tilde{\rho}^{SS}_{jk} - \tilde{\rho}_k^{SS}) \times \frac{h\gamma/2}{\pi (h\Delta_k^2)^2 + (h\gamma/2)^2} \]
where \( \bar{f}_{jk} \) is an oscillator strength per active electron.\(^{52}\) The solar flux absorption spectrum is then expressed as
\[ F(\hbar\Omega) = \alpha(\Omega) F_{\text{sol}}(\hbar\Omega)/\hbar\Omega \]
where the solar flux is approximated by the blackbody flux distribution, normalized to an incident photon flux of 1 kW/m\(^2\),
\[ F_{\text{sol}}(\hbar\Omega) = \frac{(\hbar\Omega)^3}{\pi^2 h^3} \exp(h\Omega/k_B T) - 1 \]
with \( C_T \) the flux normalization constant and the temperature \( T \) set to 5800 K.

3. RESULTS AND DISCUSSION

3.1. Reaction Pathways: CO\(_2\) Interaction with Unsupported Cu\(_5\) Clusters. Let us first analyze the interaction of CO\(_2\) with unsupported Cu\(_5\) clusters. Our results have indicated that a planar trapezoidal structure of Cu\(_5\) is only slightly energetically favored (by 0.13 eV when the energy difference is calculated with the PBE-D3(BJ) scheme) over a trigonal biplanar structure so that we have considered both. By relaxing the geometries of the Cu\(_5\) and CO\(_2\) reactants at each intermolecular Cu\(_5\)--CO\(_2\) distance, defined here as the distance between the carbon atom and the central atom of the Cu\(_5\) cluster, we obtain the interaction energies shown in the upper panel of Figure 2. Zero energy is set to having CO\(_2\) at infinite distance from the cluster. The energy pathway is characterized by a very shallow minimum of about ~0.15 eV at a long Cu\(_5\)--CO\(_2\) distance (about 5 Å) and a relatively deep potential minimum of about ~0.6 eV at a shorter distance (~3.9 Å), with a very low energy barrier in between. The shallow energy minimum emerges from a weak dispersion-dominated interaction between the two reactant species. Note that the barrier is appearing only if a bending of the CO\(_2\) molecule is allowed. Preliminary calculations of the same reaction pathway at the MP2 level of theory yield a slightly higher energy barrier (about 0.2 eV). Work is in progress to get a better estimate of the barrier to chemisorption using multireference perturbation theory, allowing us to better characterize the mixing between covalent and ionic contributions (see, for example, ref 53). An analysis of Löwdin reduced orbital charges reveals no net charge transfer between the Cu\(_5\) and CO\(_2\) species but a strong polarization of both reactant species at the energy minimum configuration. The CO\(_2\) bending gives rise to the formation of a dipole moment that interacts attractively with induced dipole and quadrupole moments formed in the polarized Cu\(_5\) cluster. From the Gibbs energies at the right-hand panel, it can be seen that the energy minimum is deep enough to “survive” at room temperature but not at temperatures higher than 100 °C.

The middle panel of Figure 2 illustrates how the adsorbed CO\(_2\) molecule, starting from its energy minimum configuration as shown in the upper panel, becomes decomposed by increasing one of the C=O distances. The planar Cu\(_5\) cluster catalyzes the CO\(_2\) decomposition, but the energetic barrier to break the CO bond is still too high (~1.3 eV) to provide a reasonable reaction rate at room temperature. The final configuration with the CO fragment attached to Cu\(_5\) is rather unstable: At about 200 °C, the asymptote for CO desorption from Cu\(_5\)--O lies approximately at the same energy as the transition state for C=O bond breaking and reduces significantly at higher temperatures due to increasing entropy.

This picture changes remarkably when considering the biplanar trigonal structure of Cu\(_5\) (bottom panel). Not only the energetic barrier of the rate-limiting step (C=O breaking) is clearly lower (~0.8 eV) but also the complex formed upon C=O breaking are very stable, as both fragments remain adsorbed at ambient temperature. Also, in contrast with the planar Cu\(_5\) counterpart, the entrance channel is characterized by a very weak interaction of the CO\(_2\) molecule with the biplanar trigonal Cu\(_5\) cluster (about ~0.3 eV). This finding once again illustrates the extreme sensitivity of atomic cluster properties with respect to structural reconformations, and it brings us straight to a final but crucial extension of our model with respect to the cluster support.
3.2. Reaction Pathways: CO$_2$ Interaction with TiO$_2$–Supported Cu$_5$ Clusters. In this section, we focus on how the CO$_2$–Cu$_5$ interaction is modified when the Cu$_5$ atomic cluster is supported on the rutile TiO$_2$(110) surface. Figure 3 summarizes the main adsorption geometries found using both the nonperiodic (left-hand panel) and periodic (right-hand panel) approaches, with the corresponding adsorption energies and main geometrical parameters summarized in Table 1. It can be seen that, with the exception of the adsorption energy for the most attractive chemisorption configuration (labeled as “4” in Table 1 and Figure 3), nonperiodic and periodic calculations provide rather similar results. The larger discrepancies in the latter case might be ascribed to the fact that the copper cluster is lying flat on the surface and therefore too close to the boundaries of the actual cluster model. This is also reflected in the larger \( d(\text{Cu–Cu}_{\text{middle}}) \) distance obtained in the periodic calculation for the physisorption configuration labeled as “2” (see Table 1) since the Ti atom becomes located close to the cluster model boundaries (see Figure 3). The discrepancies in structural parameters should be reduced upon enlargement of the cluster model. However, the next cluster size was too large for a TDDFT treatment.

When considering chemisorption configurations (labeled as “3” and “4” in Figure 3), a Bader decomposition\(^5\) shows that the Cu$_5$ cluster donates about 0.5 and 0.7 \( e \) of electronic charge to the attached CO$_2$ molecule, while the charge donation is almost negligible (below 0.02 \( e \)) when physisorption configurations are analyzed instead (labeled as “1” and “2” in Figure 3). There is a direct correlation between how much the CO$_2$ molecule becomes bent and how much electronic charge it accumulates from the Cu$_5$ cluster. In fact, upon bending, the energy of the antibonding LUMO orbital of the CO$_2$ orbital becomes lower and thus closer to that of the HOMO of the Cu$_5$ cluster, enhancing the probability of electron-transfer.

Using the finite cluster model, the upper panel of Figure 4 shows the interaction energies as a function of the intermolecular distance between the carbon atom and the central Cu atom. It can be readily observed that the interaction is strongly influenced by the support: the potential energy minimum from the surface scan is now located at a configuration with the CO$_2$ molecule physisorbed on top of one 5-fold Ti atom. As expected, with a well-depth of \(-0.33\) eV, the physisorption minimum is dominated by the dispersion component of the interaction (\(-0.24\) eV). There is almost zero net charge transfer to the CO$_2$ molecule (less than 0.02 \( e \)) but a slight polarization is occurring at the C atom. At this physisorption configuration, there is almost no bending of the CO$_2$ molecule (see Table 1). Also, a very good agreement is found between the adsorption energies and adsorption geometries obtained for the cluster and the periodic slab models of the rutile TiO$_2$(110) surface (see Table 1 and Figure 3). As can be seen in Figure 3, the physisorption nature of this configuration is also reflected in the shape of the HOMO. It is very similar to that obtained without the attached CO$_2$.

![Figure 3. Main CO$_2$ adsorption geometries on the TiO$_2$-supported Cu$_5$ cluster, using finite cluster (left-hand panel) and periodic slab (right-hand panel) models. Isodensity surfaces of the HOMOs are also shown.](image)

**Table 1. Geometry Parameters (Distances between Carbon and Oxygen Atoms, \( d \), and O–C–O Angle of CO$_2$, \( \alpha \)) and Adsorption Energies \( E_{\text{ads}} \) (in eV) (See Figure 1 for the Labeling of the Oxygen and Copper Atoms) Corresponding to the Adsorption Configurations Presented in Figure 3 for the Non-Periodic Cluster and Periodic Slab Models Shown in Figure 1**

| label | \( d(\text{O}_1–\text{C}) \) (Å) | \( d(\text{O}_2–\text{C}) \) (Å) | \( d(\text{C–Cu}_{\text{middle}}) \) (Å) | \( \alpha(\text{O}_1–\text{C–O}_2) \) (deg) | \( E_{\text{ads}} \) (eV) |
|-------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|-----------------|
| 1     | 1.18                          | 1.26                          | 4.41                           | 173                             | –0.18           | –0.22           |
| 2     | 1.17                          | 1.18                          | 3.42                           | 179                             | –0.33           | –0.28           |
| 3     | 1.25                          | 1.25                          | 3.76                           | 140                             | –0.50           | –0.39           |
| 4     | 1.21                          | 1.22                          | 2.35                           | 121                             | –1.54           | –0.82           |

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molecule (see ref 19), dominated by 4s orbitals centered on the Cu atoms, bearing also important 3p and 3d contributions. It is interesting to analyze the reasons for the adsorption energy differences which occur for the CO$_2$ molecule adsorbed on top of unsupported and supported Cu$_5$ clusters (−0.61 vs −0.22 eV). The free Cu$_5$ cluster is highly polarizable and the electronic charge becomes pushed toward the two terminal copper atoms upon the approach of the CO$_2$ molecule so that the electrostatic interaction is optimized. This polarization effect is somewhat constrained in the TiO$_2$-supported Cu$_5$ cluster since the support causes a marked redistribution of the charge (see ref 19), with the two terminal copper atoms already being negatively charged. This redistribution is only slightly modified when the CO$_2$ molecule approaches the cluster in the symmetric “on top”-configuration. A very different picture emerges if the CO$_2$ molecule is approaching from a lateral side of the Cu$_5$ cluster (see middle panel of Figure 4 and configuration labeled as “3” in Figure 3 and Table 1); in this scenario, the charge distribution on copper atoms becomes polarized toward the opposite side from the attachment of the CO$_2$ molecule. This redistribution eases the bending of the CO$_2$ molecule (even without a barrier), with the carbon atom becoming negatively charged by about −0.5 eV according to a Bader decomposition applied to the periodic model (configuration labeled as “3” in a right-hand panel of Figure 4). As a result, the adsorption energy becomes significantly lower (−0.5 eV). This adsorption energy is slightly below to that obtained considering a periodic slab model of the TiO$_2$(110) surface (−0.4 eV, see Table 1). As can be seen in Figure 3, the HOMO isodensity profile is very different from those obtained in physisorption scenarios: there is a clear mixing of orbitals of the Cu$_5$ cluster with the lowest-energy unoccupied molecular orbital (LUMO) of the free CO$_2$ molecule (i.e., the antibonding π* orbital). It is dominated by 3d components from the copper atoms, bearing also important 4s-type contributions, while carbon and oxygen atoms provide 2s- and 3d-type (carbon) and 2p-type (oxygen) contributions. Interestingly, the charge transfer to CO$_2$ in chemisorption configurations comes from the HOMO of TiO$_2$-supported Cu$_5$ and not the lowest-energy single-occupied molecular orbital (referred to as SOMO). This holds true for nonperiodic as well as periodic calculations. In fact, as analyzed in ref 19, the energy of the HOMO is very close to the bottom of the conduction band while the energy of the SOMO is about 1 eV lower (i.e., too far away from the LUMO orbital of the CO$_2$ molecule). When the system is modeled by a periodic slab, the unpaired electron from the SOMO orbital becomes localized at a 5-fold Ti ion (i.e., characterizing a small polaron Ti$^{3+}$ state). In fact, the SOMO is localized in a Ti(3d) orbital lying in the surface plane, showing no overlap with frontier orbitals of the approaching CO$_2$ molecule. This is illustrated in Figure 5.

Figure 4. Surface scans characterizing the interaction between the CO$_2$ molecule and the TiO$_2$-supported Cu$_5$ cluster. Upper panel: relaxed surface scan (RSS) as a function of the distance between the carbon atom and the central atom of the Cu$_5$ cluster (vertical approach of the CO$_2$ molecule). Middle panel: RSS as a function of the distance between the carbon atom and the center-of-mass of the Cu$_5$ cluster (lateral approach of the CO$_2$ molecule). Bottom panel: RSS as a function of one C=O distance. The nonperiodic cluster model shown in Figure 1 (left-hand panel) has been used.

Figure 5. Electronic density of states (EDOS) corresponding to the CO$_2$/Cu$_5$/TiO$_2$(110) system in the chemisorption configuration labeled as “3” in Figure 3. The insets present the SOMO and HOMO. The periodic cluster model shown in Figure 1 (right-hand panel) has been used.
presenting the electronic density of states (EDOS) together with isodensity profiles of the SOMO and HOMO. As mentioned in the introduction, as compared with closed-shell cases, the outer unpaired electrons of open-shell clusters such as the bare Cu₅ cluster are expected to be the ones shared and/or transferred to a molecular adsorbate such as CO₂. Our results clearly show that the open-shell TiO₂-supported Cu₅ cluster is a different case since the unpaired electron is localized at the small polaron Ti³⁺ state so that one of the paired electrons occupying HOMO orbitals is mainly responsible for the chemical bonding with CO₂.

Finally, the bottom panel of Figure 4 shows how the adsorption complex with a bent CO₂ molecule attached to the lateral side of the Cu₅ cluster (middle panel) evolves upon increasing of one of the C═O distances. Very remarkably, the Cu₅ cluster then prefers to lie flat on the TiO₂ support, and a rather stable adsorption CO₂/Cu₅ complex is obtained for an elongated C═O distance of about 1.4 Å. This is also clearly reflected in the mixing between Cu₅ and CO₂ orbitals, as can be observed in the HOMO isodensity profile (see the bottom panel of Figure 3). At a variance with the chemisorption state labeled as “3” in Figure 3, the carbon atom provides mostly 2s- and 2p-type orbital contributions for CO₂/Cu₅ bond formation rather than 2s- and 3d-type contributions (see above). Essentially, when the Cu₅ cluster is lying flat on the surface, the two terminal Cu atoms become bonded to in-plane oxygen ions. This feature favors the charge-transfer from the Cu₅ cluster to the attached CO₂ molecule so that the net donation becomes significantly larger (0.7 |e|). In turn, the CO₂ molecule becomes more bent than when attached to the Cu₅ cluster at the “raised” configuration (labeled as “3” in Figure 3). Notice also that the HOMO expands around the carbon atom and both copper and titanium atoms and not only the former, resulting in a stronger CO₂−Cu₅ interaction. It should be noticed that the adsorption energies calculated for the CO₂ molecule on the supported Cu₅−TiO₂ cluster are consistent with those reported by Afarzadeh et al. but considering the anatase TiO₂(010) surface and, as large as −0.64 eV²⁰ with the CO₂ molecule becoming also strongly bent (O−Cu−O angle of 129.5 deg).

Upon further increase of the C−O distance by about 2.0 Å, an energy barrier of about 0.4 eV has to be overcome. As a consequence, CO₂ decomposes into an adsorbed CO fragment, which, at longer C−O distances, eventually desorbs from the catalyst, leaving behind a single oxygen atom which remains attached to the Cu₅ cluster.

Starting with the structures of the complex in the bottom panel of Figure 4, we have realized a reoptimization using the periodic slab model of the rutile TiO₂(110) surface, allowing the atoms from the support also to relax. This way, we obtain a reaction pathway for CO₂ decomposition as shown in Figure 6. Although the values of the adsorption energies are below those obtained for the finite cluster model, the energy necessary for breaking the C═O bond is very similar (0.42 eV). The reaction pathway shown in Figure 6 highlights the occurrence of a spontaneous activation and decomposition of CO₂ on Cu₅−TiO₂. This outcome, along with the lower energy penalty (by about a factor of 3) in the rate-limiting step (C═O bond breaking), are in fact the most relevant differences when compared to the case of the unsupported Cu₅ cluster scenario.

A reaction pathway leading to CO₂ dissociation to CO has also been found for the anatase TiO₂-supported Pt₈ cluster with an energy barrier of 1.01 eV.³⁴ The enhanced catalytic activity of the Pt₈-modified TiO₂ support was also rationalized in terms of the fluxional nature of the subnanometer-sized cluster. Similarly, a reconstruction of the Pt₈ cluster was found upon CO₂ adsorption. In our case, the C−O bond is even weaker if Cu₅ cluster reconstruction is allowed. Another, very recent study investigated the nature of CO₂ adsorption on Pt₉−atomic clusters (n = 4−7) as a function of cluster size.⁵⁵ The authors found the molecule to be highly activated yet still molecularly bound, but assume dissociative adsorption for larger cluster species.

3.3. UV–Vis Absorption Spectra. 3.3.1. Cluster Model Calculations of the UV–Vis Absorption Spectra. Having analyzed the CO₂/Cu₅ and CO₂/Cu₅−TiO₂ systems in the ground electronic state, we focus now on its optical excitation. To this end, we have chosen the global minimum configuration of the unsupported CO₂/Cu₅ system (see section 3.1), with the CO₂ molecule adsorbed on top of the Cu₅ cluster (adsorption energy of about 0.6 eV). Using the cluster model of the TiO₂ surface shown in Figure 1 (left-hand panel), we first compare the TDDFT spectra for CO₂ adsorbed on unsupported and supported Cu₅ clusters.

Figure 7 (upper panel) illustrates how the irradiation of UV light onto the Cu₅ cluster (photon energies from 3.5 to 4.3 eV) is driving an electron transfer from orbitals having the higher densities on copper atoms to orbitals bearing the higher densities centered on carbon atoms. Specifically, the electron transfer process gives rise to the formation of a complex that is better characterized as the CO₂⁺−radical ion attached to the copper cluster. Preliminary calculations using the multistate complete-active-space second-order perturbation theory (CASPT2) method indicate that the well-depth of the PES in the corresponding excited ionic state is larger than 0.5 eV. As expected from the population of an orbital correlating to the SOMO antibonding orbital of the CO₂⁻fragment at the asymptotic region, the C═O bond becomes weaker than in the ground electronic state. Therefore, a higher activity for CO₂ reduction is expected upon photoexcitation.

The bottom panel of Figure 7 shows the absorption spectra of CO₂ adsorbed on the Cu₅-modified TiO₂ surface. The electron “jump” from the HOMO to an orbital with density projection on the carbon atom is evident, with the responsible peaks located at about 0.8 eV, i.e., in the infrared spectral range.
As discussed in ref 19, the HOMO of the Cu$_5$−TiO$_2$ system is dominated by 4s contributions from the copper atoms, bearing also 3p and 3d components. Essentially, the Cu$_5$ cluster donates electronic charge so that a CO$_2$•$^-$ radical attached to the Cu$_5$−TiO$_2$ composite is formed, similar to the unsupported case (see upper panel). However, as the main effect of the support, the photon energy necessary for the electronic transition is reduced by approximately 3 eV.

3.3.2. Periodic Calculations of the UV−Vis Absorption Spectra. In order to obtain a most accurate UV−vis absorption spectrum, we have used the periodic slab model of the rutile TiO$_2$(110) surface shown in Figure 1 (right-hand panel) and the RDM-DFT method as outlined in section 2.2.1, which employs the hybrid HSE06 functional. The accuracy of this methodological protocol was assessed in ref 19 for the Cu$_5$−TiO$_2$(110) system, where the theoretical photoabsorption spectra agreed very well with the experimental spectra recorded using diffuse reflectance measurements.

As shown in Figure 8, after depositing the Cu$_5$ cluster on the TiO$_2$(110) surface, the composite system presents absorption in the visible region. Furthermore, a strong enhancement of the absorption in the UV region is observed as compared with the unmodified material. The physisorption of the CO$_2$ molecule on top of the Cu$_5$ clusters modifies the spectrum profile only slightly. The major modification is observed at about 2.1 eV (blue arrows in Figure 8). As already described using the cluster approach, the transition responsible for the two additional peaks involves an electron “jump” from the HOMO so that the final state can be characterized as the CO$_2$•$^-$ radical attached to the Cu$_5$−modified surface.

4. CONCLUSIONS

In this article, we have explored the energy landscape characterizing the interaction of a CO$_2$ molecule with an unsupported or TiO$_2$-supported Cu$_5$ cluster. We further investigated the occurrence of a photoinduced charge-transfer process between the cluster and the CO$_2$ molecule. Thus, via computational modeling, we have shown how Cu$_5$ clusters catalyze the CO$_2$ decomposition by C=O bond activation and a reduction of the barrier for bond breaking. Dissociation often represents the rate-determining step in reactions involving metallic nanoparticles. When supported on TiO$_2$, C=O splitting becomes more favorable than spontaneous desorption of CO$_2$. Moreover, time-dependent DFT and RDM-DFT calculations of the UV−vis spectra indicate that the TiO$_2$-supported Cu$_5$ cluster donates electron charge to a physisorbed CO$_2$ molecule when illuminated with visible light, which is further beneficial for CO$_2$ activation.

We point out two important findings: (1) CO$_2$ can be trapped in a dispersion-dominated physisorption state and, when irradiated with visible light, is transformed into a radical CO$_2$•$^-$.

Figure 8. Photoabsorption spectra of the rutile TiO$_2$(110) surface, without adsorbates (dotted red lines), with the adsorbed Cu$_5$ cluster (dotted green lines), and with the CO$_2$ molecule physisorbed on top of the Cu$_5$ cluster (blue lines). The blue arrows indicate the position of the most intense peaks involving a transition to orbitals with high density on the carbon atom. The inset presents the orbitals involved in the photoexcitation process associated with the indicated peaks. The periodic cluster model shown in Figure 1 (right-hand panel) has been used.

Figure 7. UV−vis absorption spectra of unsupported (upper panel) and TiO$_2$-supported (bottom panel) Cu$_5$ clusters, as obtained at TDDFT level with the PBE-D3(BJ) scheme. The orbitals responsible of the most relevant transitions involving electron transfer from the Cu$_5$ cluster to the physisorbed CO$_2$ molecule are also shown. The insets present density isosurfaces of these orbitals. The nonperiodic cluster model shown in Figure 1 (left-hand panel) has been used.
Altogether, our results, along with those presented in our previous work,19 point out that TiO2-supported Cu clusters are not only innovative visible-light photoactive materials but also potential catalysts for CO2 reduction, highlighting how new catalytic and optical properties are acquired by subnanometer-sized metal clusters when deposited on technologically relevant materials. More generally, our work shows how the first-principles modeling of this new generation of ångström-sized catalysts and photocatalysts allows to understand them and, then, better control their properties. In particular, when both reactants, the metal cluster and the gas-phase molecule attached to it, are open-shell species, characterizations at a higher level of theory will become necessary, such as, e.g., those recently established by Aoiiz and collaborators.

According to our results, experimental measurements capable of detecting CO desorption from Cu5−TiO2 supported clusters as a function of temperature, with and without visible-light, would provide very useful insights regarding the conditions under which Cu5 clusters could become efficient catalysts for the removal of CO2 from the atmosphere.

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**Notes**
The authors declare no competing financial interest.

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