Tuning transition metal carbide activity by surface metal alloying: a case study on CO\textsubscript{2} capture and activation\textsuperscript{†}

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CO\textsubscript{2} is one of the main actors in the greenhouse effect and its removal from the atmosphere is becoming an urgent need. Thus, CO\textsubscript{2} capture and storage (CCS) and CO\textsubscript{2} capture and usage (CCU) are intensively investigated technologies to decrease the concentration of atmospheric CO\textsubscript{2}. Both CCS and CCU require appropriate materials to adsorb/release and adsorb/activate CO\textsubscript{2}, respectively. Recently, it has been theoretically and experimentally shown that transition metal carbides (TMC) are able to capture, store, and activate CO\textsubscript{2}. To further improve the adsorption capacity of these materials, a deep understanding of the atomic level processes involved is essential. In the present work, we theoretically investigate the possible effects of surface metal doping of these TMCs by taking TiC as a textbook case and Cr, Hf, Mo, Nb, Ta, V, W, and Zr as dopants. Using periodic slab models with large supercells and state-of-the-art density functional theory based calculations we show that CO\textsubscript{2} adsorption is enhanced by doping with metals down a group but worsened along the d series. Adsorption sites, dispersion and coverage appear to play a minor, secondary constant effect. The dopant-induced adsorption enhancement is highly biased by the charge rearrangement at the surface. In all cases, CO\textsubscript{2} activation is found but doping can shift the desorption temperature by up to 135 K.

\textsuperscript{†} Electronic supplementary information (ESI) available: Fig. S1 Top view of the (3\times2\times3)R45° model, the CO\textsubscript{2} was adsorbed both in the shown position but the dopant was moved from the near to the far position. Fig. S2 Top view of the slab model used to represent a higher coverage situation. Table S1 Bader charges on all bare surfaces. Table S2 Binding modes, and adsorption energies with and without van der Waals corrections (vdW), as obtained with PBE-D\textsubscript{3}, as well as geometry parameters, including CO\textsubscript{2} angles, C–C bond distances, \textit{d}(C–C), and CO\textsubscript{2} molecule C–O bond distances, \textit{d}(C–O). Table S3 Bader charges for all the studied surfaces with adsorbed CO\textsubscript{2}. See DOI: 10.1039/c8cp03648a

1. Introduction

Every year increasing evidence of the significant impact of global warming on the Earth is being reported.\textsuperscript{1,2} The environmental prediction models show a non-optimistic future if no urgent measures are taken to face this issue.\textsuperscript{3,4} Atmospheric CO\textsubscript{2} is one of the greenhouse gases with the highest impact, and its environmental effects are particularly problematic. Apart from well-known ones such as ocean acidification,\textsuperscript{5} there are predictions that while the anthropogenic emissions of CO\textsubscript{2} rise in the atmosphere, the CO\textsubscript{2} concentration and concomitant global warming will rise exponentially through carbon-cycle feedback.\textsuperscript{4}

Despite worldwide efforts in controlling and reducing CO\textsubscript{2} emissions, as exemplified in active environmental protocols such as Copenhagen, Kyoto, or Paris,\textsuperscript{6–8} recently the International Energy Agency (IEA), in its global energy and CO\textsubscript{2} status reports, announced an increase of 1.4% in energy-related CO\textsubscript{2} emissions.\textsuperscript{9}

Among many strategies oriented at reducing CO\textsubscript{2} emissions or at decreasing its atmospheric concentration, an appealing one is the removal of atmospheric CO\textsubscript{2} \textit{via} scrubber materials.\textsuperscript{10,11} Spurred on by the urgent requirements of the Paris protocol, CO\textsubscript{2} surface chemistry\textsuperscript{12} is experiencing a renewed interest focusing on characterizing scrubber materials and optimizing their properties in CO\textsubscript{2} capture and storage (CCS).\textsuperscript{13,14} Along this line, a desirable advance is not only in CO\textsubscript{2} capture, but its chemical activation and eventual re-use as a carbon feedstock to synthesize other valuable chemicals through the commonly known CO\textsubscript{2} capture and usage (CCU) strategies.\textsuperscript{15} Given the high CO\textsubscript{2} chemical stability, only a few privileged materials are able to selectively adsorb CO\textsubscript{2} strongly enough for CCS or CCU technologies. Moderate to high CO\textsubscript{2} adsorption energies usually indicate activation of the molecule,\textsuperscript{12} which often occurs through charge transfer from the surface of a material to the CO\textsubscript{2} 6\textalpha, anti-bonding molecular orbital, thus weakening the C–O bonds and leading to a bent geometry.\textsuperscript{10} From this point on the CO\textsubscript{2}\textsuperscript{6\textalpha} molecule is much more reactive than the neutral one and the starting point for any industrial process to reuse CO\textsubscript{2}.
From all known possible materials, transition metal carbides (TMC) have shown promising results in CO₂ capture, storage, and activation, and even conversion to valuable chemicals, while their relatively low cost makes them industrially attractive materials. Diverse density functional theory (DFT) based computational studies, mostly focused on early TMCs, proved that these materials display significant potential for CO₂ activation. In particular, TiC, WC, and especially α-Mo₂C excel among the family of TMCs, and so, have been studied in deeper detail. These TMCs have proven their CCS potential but also their CCU capabilities, as highlighted by their CO₂ based catalytic activity, including CO₂ hydrogenation towards methanol. Additional systematic DFT based studies report strong CO₂ adsorption on the most stable (001) surface of rocksalt crystal group IV (TiC, ZrC, and WC), group V (NbC, and TaC), and group VI (Mo-MoC) TMCs with concomitant activation of the adsorbed molecule, indicating that these materials may be adequate for CCU technologies.

In the search for tailor-made materials for CCS and/or CCU, different ways of tuning the surface activity towards CO₂ can be envisaged, including the use of surface doping agents. This is a common practice when considering metal and metal oxide properties, thus locally tuning the chemical activity or stabilizing certain facets as in F-doped TiO₂ nanoparticles. It has also been shown that the presence of surface dopants promotes oxygen vacancy formation on CeO₂ nanoparticles. Also, CO adsorption on ceria is easily enhanced by adding Zr or Ti in the bulk, improving CO oxidation and releasing CO₂ to the atmosphere. In the case of metals, metal alloying is a standard, but not yet fully understood or controlled, approach to modulate the surface activity. Bimetallic TMCs using earth-abundant and cheap metals, such as Fe₆Mo₆C or Ni₆Mo₆C, have been previously prepared, via stepwise reduction of precursor oxides, opening the path towards an economically reasonable synthesis procedure. Moreover, there have been clear improvements in the understanding of nanoalloys, thus opening the door to future control.

In the present work we explore transition metal doping—or surface metal alloying—on TMC surfaces in the context of CO₂ capture, storage, and activation. Here, TiC has been chosen to understand how the CO₂ adsorption energy is affected by the presence of a surface or subsurface doping agent. The dopants scrutinized are Zr, Hf, V, Nb, Mo, Cr, Ta, and W; a subset of transition metals that are known to form metal carbides. This work therefore aims to assess the significant possibility of bimetallic/doped TMCs for use in CCS and the implications for design of materials with enhanced CO₂ adsorption, following a kinetic rate balance approach successfully used in previous work of some of the authors concerning CO₂ adsorption on TMCs. Furthermore, CO₂ anchoring and activation is regarded as a first, necessary, and determining step for CO₂ conversion through CCU applications.

2. Surface models and computational details

Calculations reported in the present work have been carried out within density functional theory (DFT), using the Perdew, Burke, and Ernzerhof (PBE) implementation of the generalized gradient approximation (GGA) of the exchange–correlation functional as implemented in the Vienna Ab Initio Simulation Package (VASP). The electronic density of the valence electrons has been expanded using a plane-wave basis set with an energy cut off of 450 eV. The interactions between the core and valence electrons have been taken into account through the projector augmented wave (PAW) approach of Blöchl, as implemented by Kresse and Joubert. Atomic relaxation optimization has been carried out until forces acting on atoms were less than 0.02 eV Å⁻¹, and the electronic energy convergence is set to 10⁻⁵ eV. The convergence of the calculations has been enhanced using a Gaussian smearing method with a smearing width of 0.2 eV, yet final energies are taken extrapolated to 0 K (no smearing). The calculations are non spin-polarized. Calculations incorporating spin polarization have been performed for the pristine and doped surfaces, where the doping metal can show different spin configurations (e.g., for the Cr case, although no solutions were found with an excess of one spin) i.e. magnetic minima and the effect of spin polarization on relative energies is negligible. A Monkhorst Pack k-point sampling grid of (2×2×1) k-points has been used to carry out the necessary numerical integration in reciprocal space.

A (3√2×3√2)R45° supercell slab model has been used to represent the TiC(001) surface. The model consists of six stoichiometric atomic layers extended in the xy plane, containing eight C and Ti atoms per layer, with a vacuum gap of 15 Å in the z direction. The CO₂ molecules have been introduced 2 Å away from the surface along the z direction and different initial adsorption sites and orientations relative to the surface have been systematically sampled. The two bottom layers of the slab are fixed to simulate the bulk structure of the materials. The dopants have been placed on the surface of TiC substituting a Ti atom and considering several situations regarding the adsorbed CO₂ molecule. Given the lack of work on doped metal carbides to date, we have used a doping concentration of 3.125%, which is typical for doping concentrations in, e.g. metal oxides. All ionic relaxations were carried out using the TiC bulk optimized slab geometry. A check on the effect of further optimization of the slabs in the slab plane in which doping atoms are included results in a negligible change to the CO₂ adsorption energies which is no larger than 0.04 eV. The necessary calculations for the isolated, gas phase, CO₂ molecule, as well as for the isolated metal atoms, have been carried out in an asymmetric box of (9×10×11) Å to force correct molecular orbital occupations. In the case of isolated metal atoms, spin-polarized calculations have been carried out to correctly describe their open shell nature.

3. Results and discussion

3.1. Dopant effects on the TiC surface

The substitution of the Ti atom of the TiC(001) surface, either at the surface or subsurface atomic layers, by one atom of Cr, Hf, Mo, Nb, Ta, V, W, or Zr as a dopant has two main effects; namely surface geometry and charge density distortions. These changes
come from the differences of atomic radii and electronic configuration of the transition metal dopants relative to Ti.

For all investigated cases, the dopant at the surface site was energetically preferred over the subsurface one; differences in energies of both situations, $\Delta E_{\text{sub-surf}}$, are reported in Table 1, with generally a strong preference for dopants to be at the surface by in between circa 0.35 and 0.65 eV with exceptions for V and Ta. Given the mentioned different radii between Ti and dopant atoms, one would think that the latter can be better embedded at the surface sites than at the subsurface ones simply because lattice distortions are minimized when the dopant occupies a surface site, i.e., they are better accommodated. From this reasoning one would also expect that the closer the dopant is to Ti in the periodic table, the smaller the energetic difference between the surface and subsurface positions would be, which is indeed confirmed by the calculations reported in Table 1. The preference for substitution at surface sites may be beneficial for catalytic purposes when this situation is accompanied by a sought for chemical activity. This fact suggests that control of the TMC surface chemistry is therefore possible.

A further point to be considered is the energy cost for cation exchange, here denoted as $\Delta E_{\text{dop}}$. Table 1 reports these energies, taking isolated atoms in vacuum as the reference, where negative energies indicate stability, and reveals that not all substitutions are energetically favorable. The doping by the same group IV Zr and Hf is thermodynamically driven. Along group V (Ta, Nb, and V), doping is also thermodynamically feasible, yet gradually the stability decreases by going down a group. Finally, in group VI only Mo is energetically driven whereas Cr and W, which do not feature a rocksalt carbide, show unfavorable (positive) exchange doping energies. Thus, apparently, the ability of the TM dopant to crystallize in a rocksalt environment appears to be a determining factor.

Focusing deeper on the structural aspects, see Table 1, charge density distortions caused by the dopant are present in the neighboring C atoms only, which means that the doping clearly has a local effect. This is also observed when inspecting changes in the electron density affecting both the dopant agent and the surrounding C atoms. For instance, for the pristine TiC(001) surface, the Bader analysis for the C atoms in the outermost atomic layer predicts a charge of $-1.74$ e; a slightly larger value of $-1.90$ e in the second layer. Dopants with an oxidation state higher than Ti ($+1.74$ e), such as the extreme case of Hf, which as a surface dopant exhibits a Bader charge of $+2.03$ e, spread this charge excess over directly bonded C atoms; there are four at the surface layer with a charge of $-1.74$ e, and one subsurface C with a charge of $-1.90$ e. At the other extreme, Cr, with a charge of $+1.31$ e, implies a lower charge transfer, and, consequently, the neighboring C atoms are less negatively charged, with computed Bader charges of $-1.58$ e for surface carbon and $-1.64$ e for subsurface carbon. A complete set of calculated Bader charges for the different situations explored in the present work may be found in Table S1 of the ESI.

### 3.2. Binding modes of CO$_2$ on doped TiC(001)

A previous thorough study explored several binding modes of CO$_2$ on a set of TMC (001) surfaces and considered situations in which the molecular axis lies perpendicular or parallel to the carbide surface. Approaching of the CO$_2$ molecule to the surface in a perpendicular orientation, i.e. anchoring by one of its O atoms, results in no clear chemisorption. On the other hand, the approach of the CO$_2$ molecule with its molecular axis parallel to the surface leads to chemisorbed states, which then often lead to an activated, adsorbed, bent adsorption species. In this case, two main competitive adsorption configurations are found, both implying a bond between the CO$_2$ molecule and a surface C atom and with the O atoms nearly above the surface metal atoms. These two bonding models are the so-called TopC and MMC, see Fig. 1. However, in the presence of a doping metal, the TopC situation presents two possible conformations, TopC and TopC-adjacent, depending on the orientation of the plane formed by the atoms of the activated CO$_2$ molecule relative to the plane formed by the dopant atom, the surface C atom, and the C atom of the CO$_2$ molecule (Fig. 1). The difference here is that in TopC adjacent the CO$_2$ molecule does not have any direct interactions with the dopant site. In pristine TiC, both modes present similar binding energies (Table S2, within the accuracy of the PBE calculations, ESI†), both modes having a competitive interaction, but since the MMC mode was never preferred for any doped system, TopC was used for the forthcoming detailed exploration of the doped systems.

### 3.3. CO$_2$ adsorption strength

The CO$_2$ adsorption energy, $E_{\text{ads}}$, on the pristine or doped TiC(001) surface, is obtained as in eqn (1)

$$E_{\text{ads}} = E_{\text{Sur-CO}_2} - (E_{\text{CO}_2} + E_{\text{Sur}}),$$

where $E_{\text{Sur-CO}_2}$ is the energy of the surface with adsorbed CO$_2$, $E_{\text{Sur}}$ the energy of the clean pristine or doped TiC surface, and $E_{\text{CO}_2}$ the energy of the gas phase molecule. Within this definition, the more negative $E_{\text{ads}}$ the stronger the adsorption. From the whole set of investigated dopants, the case with Hf located in the first atomic layer exhibits the largest adsorption energy ($-0.96$ eV for TopC). This is interpreted in terms of the larger positive charge on Hf compared to Ti (see Table S1, ESI†), which induces a stronger stabilization through a coulombic Hf-O interaction as clearly seen in Fig. 2. This implies that the adsorption energies involving early TMs as dopants are larger than those involving late

### Table 1. Transition metal cation radii, C–TM distances, d(C–TM), of the surface and subsurface carbons, doping formation energies, $\Delta E_{\text{dop}}$ and PBE estimated energy differences $\Delta E_{\text{sub-surf}}$ between surface and subsurface doping sites for TM–TiC(001) surfaces

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Radius (Å)</th>
<th>d(C–TM) (Å)</th>
<th>$\Delta E_{\text{dop}}$ (eV)</th>
<th>$\Delta E_{\text{sub-surf}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{4+}$</td>
<td>0.75</td>
<td>2.17, 2.08</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.76</td>
<td>2.12, 2.16</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Hf$^{4+}$</td>
<td>0.71</td>
<td>2.22, 2.21</td>
<td>$-1.19$</td>
<td>$0.34$</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>0.73</td>
<td>2.16, 1.97</td>
<td>$-2.99$</td>
<td>$0.67$</td>
</tr>
<tr>
<td>Nb$^{5+}$</td>
<td>0.58</td>
<td>2.19, 2.07</td>
<td>$-1.26$</td>
<td>$0.39$</td>
</tr>
<tr>
<td>Ta$^{5+}$</td>
<td>0.8</td>
<td>2.18, 2.06</td>
<td>$-0.07$</td>
<td>$0.26$</td>
</tr>
<tr>
<td>V$^{5+}$</td>
<td>0.68</td>
<td>2.13, 1.93</td>
<td>$-2.33$</td>
<td>$0.26$</td>
</tr>
<tr>
<td>W$^{6+}$</td>
<td>0.51</td>
<td>2.15, 1.97</td>
<td>$0.71$</td>
<td>$0.58$</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>0.66</td>
<td>2.24, 2.26</td>
<td>$-0.68$</td>
<td>$0.62$</td>
</tr>
</tbody>
</table>
TMs (Table 2), with one of the weakest situations being W (−0.22 eV). However, the case of Ta represents an exception to this rule since even with quite a large charge of +1.91 e, it displays a slightly smaller \( E_{\text{ads}} \) (−0.57 eV) than pristine TiC. In any case, it is clear that the dopant charge is a determining factor although not the only one.

Concerning doping with W, the TopC adjacent situation implies a slightly higher adsorption energy (−0.31 eV), but this is still far from the −0.61 eV for undoped TiC. Hence, the doping effect has still a vicinal, in this case worsening, effect. The opposite applies to Hf, where TopC adjacent leads to a reduced adsorption energy of −0.81 eV. These two limiting situations (Hf and W) are selected to study the effect of dispersion and also of the proximity of the dopant to the adsorption site.

Dispersion effects are evaluated for all the examples of CO\(_2\) adsorption that we have studied (see Table S2, ESI†), using the Grimme D3 correction,\(^{39}\) as earlier studied for CO\(_2\) adsorption on TMCs.\(^{10}\) As expected, the adsorption energies increase (in absolute terms) by −0.24 up to −0.29 eV, but, more importantly, variations in this shift among the dopants are no larger than 0.05 eV. The only exception is CO\(_2\) adsorption in MMC mode on Cr–TiC where such an energy difference is −0.32 eV. Consequently, the effect of van der Waals type forces on the doping increase/decrease of the CO\(_2\) adsorption energies can be considered a constant shift and can be safely disregarded in the forthcoming discussion.

In a similar fashion, the dopant effect has been tested where the dopant is positioned farther from the CO\(_2\) than in the TopC-adjacent situation. To this end, a larger \((3\sqrt{2} \times 3\sqrt{2})\)R45° supercell is used, see Fig. S1 (ESI†). There, because of the different number of plane waves associated with the cell dimensions and the concomitant different density of \(k\)-points, the CO\(_2\) adsorption energy on undoped TiC(001) is −0.51 eV. When the CO\(_2\) is placed in the TopC situation close to Hf, the computed adsorption energy strengthens to −0.89 eV, in line with the results discussed above. However, when the CO\(_2\) is placed farther away from the Hf atom, \( E_{\text{ads}} \) becomes −0.52 eV, which is very close to that of pristine non-doped TiC. This is more clear evidence of the very local nature of the dopant effect in the carbide–CO\(_2\) interactions.

This finding can be further supported by calculations for the W doped surface with a TopC \( E_{\text{ads}} \) of −0.14 eV but −0.49 eV when CO\(_2\) is in a TopC site farther away from W, thus showing a difference of only 0.02 eV from the result for undoped TiC. In line with the above-mentioned charge density distortions (see also Table S1, ESI†), we consider in the following that the doping effect is completely local and focus on the situations where CO\(_2\) is close to the doping atom as in Fig. 1.

Finally, the same two doping agents (Hf and W) have been used to evaluate possible effects due to dopant saturation/coverage on the surface. To this end, an extra CO\(_2\) with its correspondent dopant has been added to the \((3\sqrt{2} \times 3\sqrt{2})\)R45° unit cell, effectively increasing the doping concentration and also the CO\(_2\) coverage (see Fig. S2, ESI†). The results, as expected,
reveal a reduction of the mean adsorption energies to $-0.77$ eV for the case of Hf and $-0.13$ eV for that of W. Interestingly, the local nature of the dopant effect prevails, a strengthening of the interaction is observed for Hf, and a weakening for W. The reduction with respect to the low coverage case is mostly due to steric repulsion between adsorbates.

3.4. Activated CO$_2$ structure

In all cases where the surface–CO$_2$ interaction leads to a C–C type of bond, similar structural changes appear for the adsorbed CO$_2$ molecule. The O–C–O angle is reduced from $180^\circ$ to $<130^\circ$ and the C–O distances are elongated with bond lengths in the 1.28–1.30 Å range, thus larger than the computed PBE value of 1.16 Å for CO$_2$ in vacuum (Table S3, ESI†). For the studied TopC cases, where a clear interaction exists between one of the O atoms of the CO$_2$ molecule and the dopant, the symmetry of the CO$_2$ bonds is slightly broken with the C–O distances featuring differences of up to 0.02 Å. One can speculate that this lack of symmetry might have an impact on the subsequent CO$_2$ usage since one of the C–O bonds appears to be more activated with a preference for further reactions such as CO$_2$ dissociation upon hydrogenation.

3.5. Charge transfer

Additional information to better understand the observed trends in CO$_2$ adsorption energy triggered by the presence of the dopant is gained by analyzing the net charges on relevant atoms as obtained from the Bader’s atoms-in-molecules analysis of the total electron density. To this end two possibilities are investigated involving the relationship between $E_{\text{ads}}$ and the initial Bader charges of the doped surface (Table S1, ESI†), or the net charge transfer from the doped-surface to CO$_2$ (Table S3, ESI†). The first relationship, summarized in Fig. 3, strongly supports that the more oxidized the dopant, then the stronger the adsorption of CO$_2$. This is in agreement with the previously discussed charge modifications of the surface electronic structure due to the presence of the dopant.

The chemistry behind this trend is quite simple. A more oxidized cation leads to higher negative charge on the neighboring C atoms (Table S1, ESI†) directly interacting with the adsorbate; this is a feature that favors electron transfer to the CO$_2$. On the other hand, comparing the local charges with and without the adsorption, one observes that the charge transferred to the CO$_2$ strongly depends on the binding mode rather than on the dopant (see Table S3, ESI†). Upon CO$_2$ adsorption, the surface C involved in the bonding becomes less negatively charged, and CO$_2$ is highly activated exhibiting a net charge in the $-0.76$ to $-0.98$ e range. The emerging picture of the adsorption process can be thought of as a Lewis acid–base reaction, a feature also reported for the interaction of CO$_2$ with some oxides. The surface acts as a base transferring charge to the CO$_2$ acting as an acid.

To further confirm the role played by the charge transfer in CO$_2$ adsorption on the doped TMC surfaces, the same analysis has been repeated for other binding modes with a smaller adsorption energy which all display a smaller degree of charge transfer. Thus, a general trend is present where stronger adsorption energies involve concomitant larger charge transfer, a point observed in two-dimensional carbides used in ammonia synthesis. Lastly, we note that the negatively charged adsorbate would attract other positively charged species such as H$^+$ with implications for CO$_2$ conversion, especially in its electroreduction.

3.6. Work function analysis

The bonding mechanism between doped TiC and CO$_2$ which we have discussed above and which involves charge transfer may have observable consequences. In particular, it is likely to affect the surface work function ($\phi$), a descriptor for base–acid characterization of the surfaces. Several studies, both experimental and theoretical, related to CO$_2$ adsorption on other surfaces such as Ni$^{43,44}$ and Co$^{45,46}$ evaluated this property as a chemical activity descriptor although whereas trends along a series are normally trustable$^{47}$ it needs to be used with caution.

In the present work only CO$_2$-free doped TiC(001) surfaces were studied to investigate the predictive nature of such a descriptor regarding dopant effects. Within the present surface slab model, the work function was calculated as the energy difference between the electrostatic potential in the vacuum above the surface, $V$, and the Fermi energy, $E_F$. This was carried out for the bare undoped surface model, as well as for the doped cases. A dipole correction has been applied in the direction perpendicular to the surface plane to counteract the small surface dipole created by the doping. The results for metal doped TiC(100) surfaces are summarized in Table 3. These results show that low/high work functions tend to favor/disfavor CO$_2$ adsorption, as expected. However, one must also caution that the relationship between the workfunction and CO$_2$ adsorption is not strong enough so as to conclude a definitive clear direct link between them, which is consistent with previous work.$^{47,48}$ Hence, the dopant effects appear to be too local so as to strongly modify the overall surface work function.

3.7. Adsorption/desorption rates

Pressure and temperature are important factors to control the CO$_2$ adsorption capacity of such metal doped TMCs. The rates
The obtained frequencies allow taking into account the zero point energy (ZPE) in the calculated $E_{\text{ads}}$ with values reported in Table 4. Notice that the main effect of the ZPE correction is to reduce the adsorption strength, but it does by up to, at most, 0.03 eV, and therefore can be considered negligible.

Fig. 4 reports the CO$_2$ $r_{\text{ads}}$ and $r_{\text{des}}$ values for TiC(001) and doped-TiC(001) clearly showing that a small increase in the adsorption energies implies a slight increase of the limit temperature between adsorption and desorption regions. Indeed, for Hf-doped TiC, the adsorption energy is 0.34 eV stronger than for undoped TiC(001), implying an equilibrium temperature between adsorption and desorption of 370 K; this is 135 K higher than the corresponding value for stoichiometric TiC estimated as 235 K.$^{10}$ Consequently, Hf-doped TiC would lead to CO$_2$ capture at higher temperature conditions. For other doping metals, such as W, the temperature decreases, but, in such situations, the previous analysis indicates that CO$_2$ will preferentially occupy dopant-free surface regions and, as a result, no change in the equilibrium temperature is to be expected.

### 4. Summary and conclusions

The present DFT based study reports the effects caused by a dopant in the TiC(001) surface on CO$_2$ capture, storage, and activation. The dopants considered are also early TMs (Hf, Ta, Zr, Nb, W, Cr, Mo, and V) placed either at the surface or at the subsurface layer and always replacing a Ti cation. The dopant effect on the geometric and the electronic configurations is found to be highly local. Calculations predict that doping at the outermost surface layer is always preferred over subsurface substitution. The effect of dispersion has been found to equally affect the undoped and doped situations and, therefore, can be considered as a constant. Depending on the dopant, CO$_2$ adsorption energies can be enhanced, mostly down a group, or reduced, when going along a d series.

The results reported in the present work have been obtained for doped TiC but the trends can be easily extrapolated to others TMCs. For instance, according to the observed trends, the Ti-doped VC system would feature an enhanced adsorption energy compared to pure VC. Overall, through surface doping, the CO$_2$ capture conditions can be tuned, while keeping the activated nature of the chemisorbed molecule.

A meaningful analysis of the CO$_2$ interaction with such TMCs reveals that the adsorption is driven by the surface CO$_2$ charge transfer, and ultimately biased by the surface charge rearrangement/transfer when the doping agent is introduced. We hope that the hereby predicted potential of doped TMCs for CCS and CCU technologies would trigger further experimental work in this field.

### Conflicts of interest

The authors declare no competing financial interest.
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