Two-dimensional nitrides as highly efficient potential candidates for CO₂ capture and activation†

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The performance of novel two-dimensional nitrides in carbon capture and storage (CCS) is analyzed for a broad range of pressures and temperatures. Employing an integrated theoretical framework where CO₂ adsorption/desorption rates on the M₂N (M = Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W) surfaces are derived from transition state theory and density functional theory based calculations, the present theoretical simulations consistently predict that, depending on the particular composition, CO₂ can be strongly adsorbed and even activated at temperatures above 1000 K. For practical purposes, Ti₂N, Zr₂N, Hf₂N, V₂N, Nb₂N, and Ta₂N are predicted as the best suited materials for CO₂ activation. Moreover, the estimated CO₂ uptake of 2.32–7.96 mol CO₂ kg⁻¹ reinforces the potential of these materials for CO₂ abatement.

Introduction

There is no doubt that the continuous increase in the concentration of CO₂ in the earth’s atmosphere directly correlates with global warming and that, in turn, such an increase is strongly related to anthropogenic emissions resulting from the use of fossil fuels.¹ The need to reduce the amount of this greenhouse gas has triggered research into CO₂ sequestration not only with the idea to contribute in decreasing its concentration in the atmosphere²-³ but also for its ulterior utilization as a chemical feedstock in the chemical industry. This may look as a simple idea but its practical implementation into a sufficiently large scale constitutes an enormous scientific and technological challenge.⁴ This is because of the very high stability of the gas phase CO₂, the final product of spontaneous combustion of fuels based on organic compounds such as wood, natural gas, or gasoline.

The high chemical stability of CO₂ also implies weak interaction with solid substrates, which, according to the well-known Sabatier principle, encounters problems when aiming at using heterogeneous catalysts for CO₂ conversion. Hence, in the absence of sufficiently active catalysts, CO₂ capture appears as more attractive than direct conversion. Indeed, CO₂ capture based on the amine-scrubbing technology has become a widely used method.⁵-⁶ Nevertheless, because of its non-corrosive nature, low-cost, and easy regeneration, capture by solid materials is considered as advantageous.⁷-⁸ The use of solid materials is the basis for the so-called carbon capture and storage (CCS) strategy. The requirements are similar yet less stringent than for the heterogeneous catalytic conversion.⁹ In fact, CCS requires a specific type of solid substrate that is able to adsorb CO₂ in a sufficiently strong way. Ideally, one would like to have materials being able to trigger activation usually involving charge transfer towards the molecule resulting in the generation of bent anionic CO₃²⁻ species, which are active for further reactions. Alternatively, CO₂ sequestration is feasible through carbonation of natural silicate minerals. However, it drives to the formation of carbonates (CO₃²⁻) which are chemically inert. In fact, the formation of carbonates is not desired due to the fixation of CO₂ on the substrate, making it unavailable for the subsequent conversion.¹⁰¹¹ In order to find appropriate candidates for CCS, a large number of diverse materials have been analysed involving metals, metal oxides, graphene-based materials, zeolites, metal–organic frameworks and transition metal carbides¹²-¹⁹ although with not completely satisfactory results.

The preceding discussion clearly illustrates the need to go beyond existing materials and to look for alternatives. In this sense, it is worth mentioning that an entirely new family of two-dimensional (2D) transition metal carbides and nitrides has been reported quite recently. These materials have a general Mₙ₋₁Xₙ chemical formula where M stands for early transition metals and X for C or N.²⁰²¹ Depending on n, which runs from
1 to 3, the resulting materials have 3, 5, or 7 atomic layers. Because of the similarities with graphene, including a hexagonal atomic structure, these new materials have been designated as MXenes. At present, several members of the potentially very large MXene family have been synthesized from the precursor so-called MAX phases. This was initially achieved by selectively etching Al from Ti$_3$AlC$_2$ and other Al-containing MAX phases using hydrogen fluoride. However, the progress in this field is very fast and fluorine-free synthetic procedures have recently been proposed to synthesize MXenes. Even, more recently, MXene synthesis from other MAX phases not containing Al has been achieved, which shows that the number of these materials already obtained is likely to represent a small fraction of those to be obtained in the near future. At this point it is worth pointing out that recent computational studies provide compelling evidence that these MXene materials, even the not yet synthesized materials, are mechanically and dynamically stable.

Among other properties recently reviewed, MXenes have high surface areas up to 1000 m$^2$ g$^{-1}$ and exhibit excellent stability. The high surface area displayed by MXenes together with the reactivity of transition metal carbides towards CO$_2$ adsorption and activation triggered systematic research where the CCS ability of MXenes with the M$_2$C formula has been computationally investigated. Using adsorption and desorption rates derived from transition state theory and density functional theory based calculations, it has been shown that the M$_2$C MXenes are able to adsorb and release CO$_2$ at rather high temperatures and low partial pressures. Moreover, CO$_2$ uptakes ranging from 2.34 to 8.25 mol CO$_2$ kg$^{-1}$ of substrate have been predicted, which are a direct consequence of their chemical activity and high surface area. It is worth pointing out that this uptake is equivalent to that of other porous materials used regularly for CCS purposes such as zeolites or bulk MgO nanopowders.

In the view of a very large number of potential MXene compounds and motivated by the encouraging results obtained for the M$_2$C subset, we analyse the CCS capabilities of the M$_2$N (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W) family for which information is scarce and new and their fascinating chemistry is likely to emerge. In fact, just from the higher electronic conductivity, one can already expect that their overall chemistry would be significantly different from that of their carbide counterparts. Moreover, the fact that Ti$_3$N has been already obtained and characterized can be seen as a starting point in the development of efficient synthetic routes leading to other members of the M$_2$N family.

Material models and computational methods

Models

Surface slab models were used to represent the basal (0001) plan of M$_2$N materials studied in the present work. The models were built using the crystal structure of the corresponding precursor MAX phase by removing the A element and re-optimizing both lattice parameters and fractional coordinates. The resulting slabs have three atomic layers featuring an M–N–M sandwich-like configuration as schematically shown in Fig. 1. In order to avoid the interaction between the adsorbed CO$_2$ molecules in the periodically replicated images, a p(3 × 3) supercell was used containing 18 M and 9 N atoms. Also, since the computational code used (see below) exploits the periodic symmetry in the three directions, it is necessary to add a vacuum region to avoid the interaction between the interleaved slabs; a vacuum width of 10 Å was probed to be sufficient to obtain numerically converged results.

Density functional theory based calculations

The interaction of CO$_2$ with the M$_2$N(0001) surfaces is studied by means of density functional theory (DFT) based calculations within the PBE implementation of the generalized gradient approximation (GGA) for the exchange–correlation potential. Additionally, the contribution of dispersion terms to the interaction of CO$_2$ with the M$_2$N(0001) systems is taken into account through the D3 parameterization of the method proposed by Grimme. To solve the corresponding Kohn–Sham equations, the valence electron density is expanded in a plane-wave basis set with a cut-off of 415 eV for the kinetic energy, a choice that leads to converged results up to 1 meV in adsorption energies. The interaction between the valence electron density and the core electrons is accounted for through the projector-augmented wave (PAW) method. Integration in the reciprocal space is carried out using a 5 × 5 × 1 grid of Monkhorst–Pack special k-points.

Convergence in the geometry optimization is reached when forces acting on nuclei are all below 0.01 eV Å$^{-1}$. The adsorption energy is defined as $E_{\text{ads}} = E_{\text{CO}_2/M_2N} - (E_{\text{M}_2N} + E_{\text{CO}_2}) + \Delta E_{\text{ZPE}}$, where $E_{\text{CO}_2/M_2N}$ corresponds to the energy of CO$_2$ adsorbed on the M$_2$N surface and $E_{\text{M}_2N}$ stands for the energy of the relaxed pristine M$_2$N surface; $E_{\text{CO}_2}$ corresponds to the energy of an isolated CO$_2$ molecule computed in a symmetric box of $10 \times 10 \times 10$ Å dimensions and using the Γ-point only. Finally, $\Delta E_{\text{ZPE}}$ corresponds to the difference in the zero-point energy (ZPE) of each term contribution calculated in the harmonic approximation. Note that the vibrational frequencies were calculated decoupled from surface phonons and including frustrated rotations/translations. Attending to this definition of $E_{\text{ads}}$, adsorption is associated with negative values, and the more the negative the stronger the interaction. All DFT based calculations are performed with the Vienna Ab initio Simulation Package (VASP).

Adsorption/desorption rates

Assuming that CO$_2$ adsorption is a non-activated process, a meaningful choice, the adsorption rate $r_{\text{ads}}$ can be calculated from the well-known Hertz–Knudsen formula as in eqn (1),

$$r_{\text{ads}} = \frac{S_0 \cdot p_{\text{CO}_2} \cdot A}{\sqrt{2 \pi \cdot m \cdot k_B \cdot T}}$$

where $S_0$ is the initial sticking coefficient, $p_{\text{CO}_2}$ corresponds to the CO$_2$ partial pressure above the surface, $A$ stands for the area of an active adsorption site and $m$ corresponds to the mass of the adsorbed molecule. A conservative value of...
$S_0 = 0.40$ is selected for our study following a previous analysis where the CO$_2$ capture, storage, and activation were investigated on transition metal carbides and two-dimensional M$_2$C MXenes.\textsuperscript{18,28} This sticking coefficient corresponds to a very conservative value corresponding to CO$_2$ on clean metal surfaces\textsuperscript{43} and thus represents a quite negative scenario. Note that the equal adsorption probability of all sites (Fig. 1) is assumed, and therefore, $A$ is approached as the supercell area of each surface divided by the total number of adsorption sites in it. Three different pressure values representative of different conditions of interest are selected to evaluate $r_{\text{ads}}$: (i) the atmospheric partial pressure of CO$_2$, $p_{\text{CO}_2} = 40$ Pa,\textsuperscript{44} (ii) a partial pressure of $p_{\text{CO}_2} = 0.15$ bar ($15 \times 10^5$ Pa), which is a reference value for post-combustion exhaust gases;\textsuperscript{45} and (iii) a partial pressure of $p_{\text{CO}_2} = 1.0$ bar ($10^5$ Pa) corresponding to a reference for pure CO$_2$ stream generation from a carbon capture and storage (CCS) system.\textsuperscript{46}

The rate of desorption, $r_{\text{des}}$, has been estimated from transition state theory (TST),\textsuperscript{47} stating that the reaction rate $r_i$ of an elementary step is given by

$$r_i = v \cdot \exp\left(\frac{-\Delta E}{k_B \cdot T}\right); \quad v = \frac{k_B \cdot T \cdot q^\text{gas} \cdot q^\text{rot} \cdot q^\text{vib}}{h \cdot q_0},$$

(2)

where $k_BT$ is the product of the Boltzmann constant $k_B$ and the temperature $T$ and $\Delta E$ would be associated with the zero-point corrected energy barrier for the described elementary step, here using the (negative) $E_{\text{ads}}$ values, which imply that the transition state is supposed to be located infinitely close to the desorption final state. In eqn (2), $v$ is the well-known pre-exponential factor term also provided by TST with $h$, $q^\text{gas}$ and $q_0$ being the Planck constant, and the partition functions of the transition and initial states, respectively. Hence one has

$$r_{\text{des}} = v_{\text{des}} \cdot \exp\left(\frac{E_{\text{ads}}}{k_B \cdot T}\right); \quad v_{\text{des}} = \frac{k_B \cdot T \cdot q_{\text{gas}}^\text{trans,2D} \cdot q_{\text{rot}}^\text{gas} \cdot q_{\text{vib}}^\text{gas}}{q_{\text{vib}}^\text{ads}},$$

(3)

where $v_{\text{des}}$ consists of the partition function of the molecule in an early 2D transition state in the numerator. This partition function is given by the product $q_{\text{gas}}^\text{trans,2D} q_{\text{rot}}^\text{gas} q_{\text{vib}}^\text{gas}$ in which $q_{\text{gas}}^\text{trans,2D}$ stands for the partition function for translational motion in two dimensions, whereas $q_{\text{rot}}^\text{gas}$ and $q_{\text{vib}}^\text{gas}$ correspond to the rotational and vibrational partition functions of the CO$_2$ molecule in the gas phase, respectively. Once the molecule is adsorbed on the surface, all degrees of freedom are considered as vibrations since molecular translations and rotations become frustrated through the interaction with the substrate and effectively converted into vibrations. The $q_{\text{vib}}^\text{ads}$ partition function contains vibrational contributions only. Finally, note
that the electronic partition function is set to 1, which is justified by the high energy of the excited electronic states. Therefore, the necessary partition functions were evaluated as

$$q_{\text{gas}}^{\text{trans,2D}} = A \cdot \frac{2\pi \cdot k_B \cdot T}{h^2}, \tag{4}$$

$$q_{\text{ads/gas}}^{\text{vib}} = \prod_i \frac{\exp \left( -\frac{h \cdot v_i}{k_B \cdot T} \right)}{1 - \exp \left( -\frac{h \cdot v_i}{k_B \cdot T} \right)}, \tag{5}$$

$$q_{\text{rot}}^{\text{gas}} = \frac{T}{2 \cdot T_{\text{rot}}}, \tag{6}$$

where $v_i$ is the harmonic vibrational frequency of each normal mode as predicted from the present DFT based calculations, for the CO2 molecule either in a vacuum or being adsorbed, and $2T_{\text{rot}}$ is the product of the rotational temperature for CO2 and its symmetry number, $2$. $T_{\text{rot}}$ is taken from the literature as 0.561 K.\textsuperscript{48}

### Results and discussion

One of the main goals of the present study is to provide qualitative and quantitative information regarding the interaction—and possible activation—of CO2 with M$_2$N(0001) surfaces. To this end, a systematic computational search has been launched considering different orientations of the CO2 molecule with respect to the surface plane and taking a wide range of possible adsorption sites into account. The final atomic structure of the adsorbed CO2 molecules predicted by the geometry optimization using an appropriate DFT based method reduces to eight particular sites and the explored M2N systems display at least one of these configurations. To distinguish among these eight bonding modes, a notation is used in which the first digit [$n$] is assigned depending on the number of atoms of the CO2 molecule (1, 2, or 3) close enough to the surface ($n$-CO2). Clearly, this depends on the orientation of the adsorbed CO2 molecule as clearly seen in the side view in Fig. 1. The notation uses a second digit ($m$) describing the atomic environment (2, 3, 4, or 5) of the adsorbed CO2 molecule ($\mu$) and ends by a specification of the location of the $n$ surface atoms in contact with the CO2 molecule (N, M, or B which correspond to nitrogen hollow, metal hollow, or bridge sites). Hence, the eight different bonding modes are univocally labelled as follows: $\eta^1$-CO2$^2\mu^2$-CB, $\eta^1$-CO2$^2\mu^4$-C$_2$MOB, $\eta^2$-CO2$^2\mu^1$-C$_2$NOB, $\eta^3$-CO2$^2\mu^2$-C$_3$MOB, $\eta^3$-CO2$^2\mu^2$-C$_3$NOB, $\eta^1$-CO2$^2\mu^2$-C$_4$MOB, $\eta^2$-CO2$^2\mu^1$-C$_4$NOB, and $\eta^3$-CO2$^2\mu^2$-C$_5$MOB. Also note that whether a given bonding mode appears or not depends on each particular M$_2$N surface. For instance, O$_8$MOB and C$_5$MOB are only found in Ta$_2$N and W$_2$N. However, in most cases (Hf$_2$N, V$_2$N, Nb$_2$N, Ta$_2$N, Cr$_2$N, Mo$_2$N, and W$_2$N), C$_9$ is the most favourable bonding mode for CO2 adsorption. It is worth pointing out that this bonding mode was also found to be the second most favourable one for the interaction of CO2 with the related M$_2$C series of MXenes.\textsuperscript{24} Note, however, that the structural features of the M$_2$N materials here studied lead to the sites for CO2 that are more accessible than those of their carbide counterparts.

The analysis of the results in Table 1 shows that the PBE-D3 calculated adsorption energy ($E_{\text{ads}}$) values are quite large ranging from $-1.03$ (Mo$_2$N) to $-3.13$ eV (Ti$_2$N)\textsuperscript{18}, indicating a very strong interaction. Interestingly, these values are only slightly smaller than those reported at the same computational level for their M$_2$C counterparts running from $-1.13$ to $-3.69$ eV.\textsuperscript{28} This origin of this difference is quite simple to understand, the N layer in the M$_2$N systems withdraws more charge density from the metal layers than the C layer in the M$_2$C ones, implying a reduction in the charge transfer from the metallic layer of the MXene towards CO2. Table 1 also shows that $E_{\text{ads}}$ generally decreases (less negative values indicate weaker adsorption) when moving along the $d$ series, which is consistent with the trends reported for CO2 adsorption on several M$_2$C and M$_2$C$_2$ systems.\textsuperscript{18,28,49} One remarkable difference between M$_2$C and M$_2$N systems is the importance of the contribution of dispersion terms to $E_{\text{ads}}$. The inclusion of these terms through the D3 Grimme method increases the PBE calculated $E_{\text{ads}}$ (in absolute terms) for M$_2$N materials by quite a significant amount (0.7–1.0 eV) where a smaller contribution of $\sim$0.40 eV was found for the studied M$_2$C compounds. One could argue that the larger contribution for M$_2$N materials arises from artefacts in the empirical parameters entering in the D3 methods. To rule out this possibility, calculations have also been carried out with the better theoretically grounded Tkatchenko-Scheffler (TS)\textsuperscript{50} approach or the more sophisticated surface many-body dispersion (MBD) approach.\textsuperscript{51} For V$_2$N, the calculated D3 contribution to $E_{\text{ads}}$ is $-0.69$ eV, in full agreement with values of $-0.68$ and $-0.71$ eV as predicted from TS and MBD methods, respectively (additional details regarding these issues can be found in the ESI†). This unexpected important contribution of dispersion terms up to 1 eV has significant implications in the temperature range at which CO2 desorbs, which we discuss in more detail later. Here we note that, in spite of the strong interaction, the geometry optimization procedure always converges to some of the molecularly adsorbed states described above with no evidence of dissociative chemisorption, indicating that this would take place at an energy barrier that would have to be overcome. Interestingly, a bent adsorbed CO2 molecule is found in most cases with the O–C–O angle in the 111–137° range and the C–O bond distances in the 1.25–1.44 Å interval, significantly larger than

<table>
<thead>
<tr>
<th>MXene</th>
<th>$E_{\text{ads}}$ (eV)</th>
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<tr>
<td>d$^2$</td>
<td></td>
</tr>
<tr>
<td>Ti$_2$N</td>
<td>$-3.13$ (C$_9$O$_8$O$_9$)</td>
</tr>
<tr>
<td>Zr$_2$N</td>
<td>$-2.97$ (C$_9$O$_8$O$_9$)</td>
</tr>
<tr>
<td>Hf$_2$N</td>
<td>$-2.97$ (C$_9$O$_8$O$_9$)</td>
</tr>
<tr>
<td>d$^3$</td>
<td></td>
</tr>
<tr>
<td>V$_2$N</td>
<td>$-1.67$ (C$_9$)</td>
</tr>
<tr>
<td>Nb$_2$N</td>
<td>$-1.73$ (C$_9$)</td>
</tr>
<tr>
<td>Ta$_2$N</td>
<td>$-1.90$ (C$_9$)</td>
</tr>
<tr>
<td>d$^4$</td>
<td></td>
</tr>
<tr>
<td>Cr$_2$N</td>
<td>$-1.44$ (C$_9$O$_8$O$_9$)</td>
</tr>
<tr>
<td>Mo$_2$N</td>
<td>$-1.34$ (C$_9$O$_8$O$_9$)</td>
</tr>
<tr>
<td>W$_2$N</td>
<td>$-2.59$ (C$_9$O$_8$O$_9$)</td>
</tr>
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the value for the isolated gas phase molecule. The chemical activation of adsorbed CO$_2$ is additionally confirmed by the net charge computed using the Bader atoms-in-molecules analysis,

indicating the formation of highly anionic adsorbed CO$_2$ species with charges running from −0.86 to −2.02 e. The results discussed so far support the claim that M$_2$N systems are appropriate for CO$_2$ activation.

The very large adsorption energy and concomitant activation of CO$_2$ on M$_2$N(0001) surfaces strongly suggest that CO$_2$ may be adsorbed up to quite high temperatures. Making use of the above-described theoretical framework, $r_{\text{ads}}$ and $r_{\text{des}}$ rates are estimated for a broad range of temperatures as high as 2000 K.

Although the upper limit corresponds to a very high temperature it is below the melting point of the corresponding 3D transition metal nitrides, ranging from 2350 to 3330 K.$^{53,54}$ Obviously, the adsorption rate has a non-negligible dependence on the number of CO$_2$ molecules hitting the surface and thus on the CO$_2$ partial pressure ($p_{\text{CO}_2}$). Also, the desorption rate is determined by the adsorption energy which in turn depends on the bonding mode (Table 1). Hence, two desorption curves for each M$_2$N have been built which differ on whether the PBE or PBE-D3 $E_{\text{ads}}$ value is used. This choice allows one to consider the least and most favourable adsorption situations, thus avoiding any bias from the choice of a given computational method and providing a
reasonable range of values for subsequent analysis. The estimated \( r_{\text{ads}} \) and \( r_{\text{des}} \) are illustrated in Fig. 2a for M\(_2\)N systems with the lowest (Cr\(_2\)N) and highest (Ti\(_2\)N) \( r_{\text{ads}} \) values (see also Table 1 and Table S1 in the ESI†). Note that two sites (C\(_3\)dO\(_3\)O\(_3\) and C\(_8\)dO\(_8\)O\(_8\)) with similar adsorption strength are found for Ti\(_2\)N and, hence, only an estimated \( r_{\text{des}} \) including PBE and PBE-D3 is expected for this MXene as reported in Fig. 2a.

Let us now describe in detail the features of the plots of adsorption/desorption rates shown in Fig. 2a. The crossing point between \( r_{\text{ads}} \) and \( r_{\text{des}} \) indicates the dynamical equilibrium state where the adsorption and desorption rates coincide, temperatures below the crossing point favour adsorption and, consequently, CO\(_2\) becomes sequestered at the material surface. For the case of Cr\(_2\)N at 40 Pa \( p_{\text{CO}_2} \) (labelled as air), two intersections at temperatures of 106 and 579 K are clearly seen corresponding to the weakest (PBE) and strongest (PBE-D3) estimates, respectively. In this way, \( T_1-T_2 \) defines the temperature range below which CO\(_2\) adsorption dominates and, consequently, it would become stored on the M\(_2\)N surface above this temperature desorption will prevail and CO\(_2\) will be released to the gas phase. Note that an increase of \( p_{\text{CO}_2} \) to \( 15 \times 10^3 \) Pa shifts these limits to the \( T_2-T_3 \) interval corresponding to higher values, and this is even further increased at 1 bar pressure as indicated by the \( T_3-T_4 \) interval. Note that these temperature ranges are quite large for Cr\(_2\)N and W\(_2\)N, and this is mainly due to the significant high contribution of dispersion terms (PBE-D3 value) to the adsorption energy value. The average adsorption/desorption switch temperature for the whole set of M\(_2\)N surfaces explored in the present work is \(~1000\) K (see Fig. 2b). Interestingly enough, this appears to be quite below the average value for their M\(_2\)C counterparts where this occurs at \(~1250\) K.\(^{28}\)

The above discussion applies to every M\(_2\)N surface studied and the analysis of the rest of the cases is summarized in Fig. 2b where the temperature ranges are shown, independent of the particular adsorption energy and rate. Further information is provided in Table S3 in the ESI† including details regarding the temperature range for each particular site of each of the M\(_2\)N surfaces. From Fig. 2b, it also appears that M\(_2\)N materials with high adsorption energies feature elevated temperature ranges. Therefore, Ti\(_2\)N, Zr\(_2\)N, and Hf\(_2\)N (d\(^3\) MXenes) display the largest temperature ranges, whereas Cr\(_2\)N, Mo\(_2\)N, and W\(_2\)N (d\(^1\) MXenes) feature the smallest. The present results strongly suggest that, for practical purposes, d\(^3\) and d\(^1\) nitride MXenes (Ti\(_2\)N, Zr\(_2\)N, Hf\(_2\)N, V\(_2\)N, Nb\(_2\)N, and Ta\(_2\)N) are among the most appealing materials for CO\(_2\) abatement. This is reinforced by the fact that adsorption/desorption transitions under air conditions are located near or within room temperature. Indeed, the M\(_2\)N materials show a larger adaptability than the M\(_2\)C counterparts, where only Mo\(_2\)C and W\(_2\)C meet this criterion.

To further examine the capability of the M\(_2\)N materials to store CO\(_2\), we focus on the total amount of this compound that can store CO\(_2\) per kg of substrate and then compare it to the values for different families of materials that have been successfully proved such as Ca-X and 13X zeolites,\(^{29,30}\) with 3.36 and 3.96 mol CO\(_2\) kg\(^{-1}\), respectively, or derivatives of graphene, e.g. a-RGO-950\(^{31}\) with 3.36 mol CO\(_2\) kg\(^{-1}\), which are clearly better than using bulk MgO nanopowders,\(^{33}\) with 0.92 mol CO\(_2\) kg\(^{-1}\). To model the potential amount of CO\(_2\) storage by the M\(_2\)N materials, we take into account the surface exposure and possible CO\(_2\) loading to the high surface area exposed by 2D MXenes.\(^{23}\) For the p(3 \times 3) supercell model employed in this study, one can safely argue that each M\(_2\)N surface could simultaneously adsorb four CO\(_2\) molecules. From this quite a conservative estimate, one readily predicts that the M\(_2\)N compounds studied in the present work would be able to adsorb 2.32–7.96 mol CO\(_2\) kg\(^{-1}\) of substrate (Fig. 3). Clearly, practical operating conditions would require CO\(_2\) separation from other competing (combustion) gases prior to adsorption, although

![Fig. 3 Predicted CO\(_2\) uptake by M\(_2\)N materials compared to values in the literature for zeolites (Ca-X and 13X), derivatives of graphene (a-RGO-950) and bulk MgO nanopowders is represented in dark blue, red, light blue, and dark yellow bars, respectively. Details are given in the ESI.†](image-url)
recent studies on a series of 2D (MXenes) and 3D transition metal carbides show a high adsorption preference for CO₂ with respect to other gases such as CO or CH₄ by more than 1.5 eV.55,56

Conclusions

The computational modelling presented in this study, based on state-of-the-art DFT-based calculations and the use of transition state theory derived adsorption/desorption rates, highlights the potential of 2D M₂N materials (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W) for CO₂ storage and activation. Our study reports high adsorption energies up to −3.13 eV accompanied by a noticeably large CO₂ activation, evidenced by the appearance of a strongly anionic CO₃²⁻ adsorbed species with elongated δ(CO) bonds, bent structures, and significant MXene→CO₂ charge transfer. The high adsorption energies are remarkable since one must point out that CO₂ adsorbs very weakly on most of the materials. The significantly large adsorption energy value for CO₂ on the M₂N materials makes them even more suitable than their carbide (M₂C) counterparts, indicating that M₂N materials may constitute effective alternatives for efficient CO₂ capture, storage, and activation. This is supported by the temperature ranges for adsorption/desorption switching and by predicted CO₂ uptakes ranging from 2.32 to 7.96 mol CO₂ kg⁻¹ of substrate, quite competitive to other nowadays existent material solutions. Finally, the fact that CO₂ becomes highly activated suggest that these 2D M₂N MXenes could also constitute active catalysts for CO₂ conversion although this requires additional research. We hope the present results will stimulate further research on the synthesis of new members of the M₂N family as well as experimental studies regarding their CCS capability.

Conflicts of interest

There are no conflicts to declare.

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