Electronic supplementary information (ESI)

Thickness Biased Capture of CO₂ on Carbide MXenes

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S1. Reaction Rate Estimates

A procedure to evaluate the Carbon Capture and Storage (*CCS*) capabilities of MXenes is to evaluate the CO₂ rates of adsorption (r_{ads}) and desorption (r_{des}), easily obtained from Transition State Theory (*TST*),^{1,2}

$$r_i = v \cdot exp\left(-\frac{\Delta E}{k_B T}\right); \ v = \frac{k_B T q^{\#}}{h \ q_0}$$
(1),

where k_BT is the product of Boltzmann constant, k_B , and temperature, *T*. ΔE would be the energy barrier for the *i*th described transition process. In Eq. (1) v is the prefactor term obtained from TST with *h* being the Planck constant, whereas $q^{\#}$ and q_0 stand for the partition function of the transition and initial states, respectively.

The r_{ads} for a non-activated adsorption depends on the impingement of adsorbates on the surface and defines,

$$r_{ads} = \frac{S_0 p_{CO_2} A}{\sqrt{2\pi m k_B T}}$$
(2),

where S_0 is the initial sticking coefficient, ${}^{p_{CO_2}}$ the CO₂ partial pressure, A stands for the area of an adsorption site, and m corresponds to the mass of the CO₂ molecule. Commonly, when unknown, initial sticking coefficients are set to unity, assuming a mobile physiosorbed precursor rate.¹ However, reported initial sticking coefficients were found to be in the range of 0.43–0.73 for CO₂ on clean metal surfaces,³ which seem more realistic. Here we used the conservative value of $S_0 = 0.40$ as used in the past.⁴ Equal adsorption probabilities of all sites were assumed, and A was therefore calculated by dividing the unit cell area of each surface by the total number of sites in it. Three representative operative conditions of CO₂ partial pressure (${}^{p_{CO_2}}$) are highlighted, including the atmospheric partial pressure of CO₂ (air), ${}^{p_{CO_2}} = 40$ Pa;⁵ a partial pressure which is a reference value for post-combustion exhaust gases (exhaust), ${}^{p_{CO_2}} = 15 \cdot 10^3$ Pa;⁶ and a reference value for pure CO₂ stream generation from a CCS system (desorption), ${}^{p_{CO_2}} = 10^5$ Pa.⁷

The r_{des} is obtained from the adsorption energy (E_{ads}) values, Zero Point Energy (*ZPE*) corrected. It is worth pointing out that $E_{ads} = -E_{des}$. Thus, E_{ads} is considered in Eq. (3),

$$r_{des} = v_{des} \cdot exp\left(\frac{E_{ads}}{k_B T}\right); \ v_{des} = \frac{k_B T q_{trans,2D} q_{rot}^{gas} q_{vib}^{gas}}{h \quad q_{vib}^{ads}}$$
(3),

where the prefactor for desorption, v_{des} , contains the partition function of the molecule in an early 2D transition state in the numerator. This partition function is given by the product $q_{trans,2D}^{gas}q_{vib}^{gas}$, in which $q_{trans,2D}^{gas}$ is the partition function for translational motion in two dimensions, and q_{rot}^{gas} and q_{vib}^{gas} are the rotational and vibrational partition functions in the gas phase, respectively. In the adsorbed state of the molecule all degrees of freedom are treated as vibrations —since molecular translations and rotations become frustrated by the substrate, and so, effectively converted into vibrations, and the partition function q_{vib}^{ads} in the denominator of v_{des} therefore only contains vibrational contributions. It should be mentioned that the electronic partition function was set to 1 given that excited electronic states lie high in energy. The partition functions have been evaluated as

$$q_{trans,2D}^{gas} = A \frac{2\pi m k_B T}{h^2}$$

$$q_{vib}^{ads/gas} = \prod_i \frac{1}{1 - \exp\left(-\frac{hv_i}{k_B T}\right)}$$
(4),

(5),

$$q_{rot}^{gas} = T/(T_{rot} \cdot 2) \tag{6}$$

where v_i is the vibrational frequency of each normal mode as obtained from our DFT calculations, either for CO₂ in vacuum or adsorbed. Note that Eq. 5 corresponds to the situation for which the adsorption energy is ZPE corrected. T_{rot} is the product of the rotational temperature for CO₂ and its symmetry number 2. From the literature the value T_{rot} is taken as 0.561 K.⁸

The T-dependent adsorption/desorption rates see Fig. S1, lead to identify the range of temperatures at which the adsorption prevails and, consequently, the CO₂ gets stored on the studied substrate. The crossing point between r_{ads} and r_{des} , shown in Fig. S1, takes place at a certain temperature labelled as T_1 . Below such temperature the adsorption is favorable ($r_{ads} > r_{des}$) and, therefore, the CO₂ is stored. On the other hand, the region located at temperatures above T_1 correspond to a process of favorable desorption ($r_{ads} < r_{des}$). One step further consists in the design of the kinetic phase diagram based on the equilibrium region where both rates are equal ($r_{ads} = r_{des}$) at a certain temperature, T_1 . Note that r_{ads} depends on Eq. 2 and, therefore, we can represent different r_{ads} corresponding to different ${}^{p_{CO_2}}$ —see the right panel of Fig. S2. By doing this, we can analyze several equilibrium regions that are characterized by different value of T and ${}^{p_{CO_2}}$. Such set of

values allow us constructing the kinetic phase diagram depicted in the right panel of Fig. S2. The solid line depicted in the kinetic phase diagram stands for the CCS–to–non-CCS crossover and, hence, the region located in the left side corresponds to the *T* and p_{CO_2} conditions at which the CCS is kinetically favorable, and the left side from the line indicates the non-CCS. It is worth to point out that p_{CO_2} can be estimated as a function of temperature under the $r_{ads} = r_{des}$ condition by,

$$p_{CO_2} = \frac{\sqrt{2\pi m k_B T}}{S_0 A} \cdot \frac{k_B T}{h} \cdot \frac{q_{trans,2D} q_{rot}^{gas} q_{vib}^{gas}}{q_{vib}^{ads}} \cdot exp\left(\frac{E_{ads}}{k_B T}\right)$$
(7).

Following the abovementioned strategy, we were able to build kinetic phase diagrams for all MXene and metal carbide surfaces investigated in this study, as depicted in Fig. S3.

Fig. S1 General scheme of calculated rates for adsorption (r_{ads}) and desorption (r_{des}) of CO₂ on a given substrate.



Fig. S2 Diagram of adsorption/desorption rates along with its transformation into a kinetic phase diagram.



S4

Fig. S3 Kinetic phase diagrams for the studied (0001) $M_{2n+1}C_n$ MXenes and the (001) and (111) surfaces of the equivalent transition metal carbides (M=Ti, Zr, Hf, V, Nb, Ta, Mo, and W). The isobars of the current CO₂ atmospheric partial pressure (air, $p_{CO_2} = 40$ Pa), that at post-combustion exhaust gases (exhaust, $p_{CO_2} = 15 \cdot 10^3$ Pa), and a reference value for pure CO₂ stream generation (desorption, $p_{CO_2} = 10^5$ Pa) are shown by white dashed dot lines.



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