

Transition Metal Carbides as Novel Materials for CO₂ Capture, Storage, and Activation

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Computational Details:

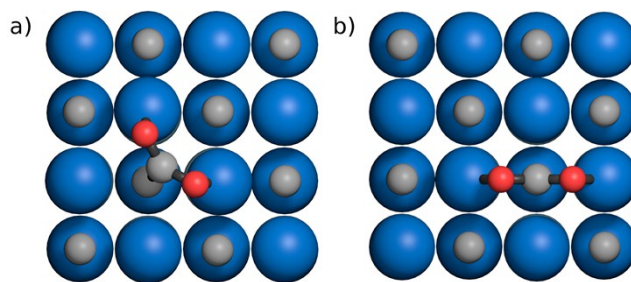
Periodic Density Functional Theory (DFT) calculations have been carried out using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,¹ and also by adding to it the D3 dispersion correction as proposed by Grimme (PBE-D3).² Core electrons were described by the projected augmented wave method of Blöchl³ as implemented by Kresse and Joubert.⁴ The valence electron density was expanded in a plane wave basis set with a cut-off energy of 415 eV. A Monkhorst-Pack **k**-point scheme⁵ of 9×9×1 dimensions. The threshold for the electronic optimization was set to 10⁻⁵ eV, and geometry optimizations considered converged when forces acting on atoms were below 0.01 eV Å⁻¹. The slab models for the Transition Metal Carbide (TMC) surfaces were built from the optimized bulk unit cell and contained four atomic layers, each containing 8 TM and 8 C atoms. The two top atomic layers were allowed to relax before and remained unfixed in the course of CO₂ adsorption — (2+2) approach—. A vacuum of 10 Å was inserted between the slabs to avoid interactions between slabs. CO₂ molecule with a C-O distance of 1.176 Å was initially placed parallel to the surface above the sampled site. These approaches already proved suitable for the description of bulk structure, (001) surfaces, and adsorption processes of the investigated TMCs in earlier studies.⁶⁻⁹ Here adsorption energy, E_{ads} , is defined as:

$$E_{ads} = E_{CO_2/slab} - (E_{slab} + E_{CO_2}) + E_{ZP} \quad (1)$$

where $E_{CO_2/slab}$ is the energy of CO₂ adsorbed on the corresponding TMC slab model, E_{slab} is the energy of the relaxed pristine slab, E_{CO_2} is the energy of an isolated CO₂ molecule, calculated at the Γ -point in an asymmetric box of 9×10×11 Å dimensions, and E_{ZP} is the zero point energy of CO₂ in the harmonic approximation. Note that ZP is considered for both gas phase and adsorbed CO₂. For the latter, vibrational frequencies were calculated decoupled from surface phonons, and including frustrated rotations/translations. With this definition, the more negative the E_{ads} , the stronger the adsorption. The obtained energy minima have been characterized by frequency analysis from the eigenvalues of the Hessian Matrix.

Table S 1: Results of CO₂ adsorption on different TMC(001) surfaces, on MMC and TopC sites, as calculated at PBE and PBE-D3 levels. The C-C, C-O, and TM-O bond lengths, *d*, are given in Å, as well as the CO₂ molecular angle, α , in degrees.

Surface	Functional	Site	$E_{\text{ads}}/\text{eV}^{\text{a}}$	$d(\text{C-C})/\text{Å}$	$d(\text{C-O})/\text{Å}$	$\alpha(\text{OCO})/^{\circ}$	$d(\text{TM-O})/\text{Å}$
TiC(001)	PBE	MMC	-0.55	1.50	1.29	122.6	2.09
	PBE-D3	MMC	-0.81	1.50	1.29	122.6	2.09
	PBE	TopC	-0.57	1.49	1.29	127.4	2.23
	PBE-D3	TopC	-0.83	1.48	1.29	127.5	2.23
ZrC(001)	PBE	MMC	-1.34	1.46	1.31	122.5	2.29
	PBE-D3	MMC	-1.56	1.46	1.31	122.6	2.29
	PBE	TopC	-1.39	1.47	1.30	124.1	2.33
	PBE-D3	TopC	-1.60	1.47	1.30	124.2	2.33
HfC(001)	PBE	MMC	-1.38	1.48	1.31	120.9	2.19
	PBE-D3	MMC	-1.62	1.48	1.31	120.9	2.18
	PBE	TopC	-1.42	1.47	1.30	124.7	2.29
	PBE-D3	TopC	-1.65	1.47	1.30	124.8	2.29
NbC(001)	PBE	MMC	-0.59	1.47	1.31	121.3	2.18
	PBE-D3	MMC	-0.87	1.47	1.31	121.4	2.18
	PBE	TopC	-0.41	1.48	1.29	127.6	2.37
	PBE-D3	TopC	-0.70	1.47	1.29	127.7	2.37
TaC(001)	PBE	MMC	-0.95	1.45	1.32	119.9	2.12
	PBE-D3	MMC	-1.21	1.46	1.32	120.1	2.13
	PBE	TopC	-0.67	1.46	1.30	127.9	2.31
	PBE-D3	TopC	-0.94	1.46	1.30	128.0	2.31
δ -MoC(001)	PBE	MMC	-0.89	1.46	1.30	121.1	2.15
	PBE-D3	MMC	-1.20	1.46	1.30	121.1	2.15
	PBE	TopC	-0.71	1.46	1.29	128.8	2.36
	PBE-D3	TopC	-1.03	1.46	1.29	128.7	2.36

^a Zero point corrected as above stated.**Figure S 1:** Top sketches of CO₂ adsorbed on a) MMC and b) TopC sites of TiC(001) surface. Atom coloring as in Figure 1 of the communication.

Calculation of adsorption/desorption rates:

For a first estimate we used DFT results and the equation for an elementary reaction rate r_i obtained from Transition State Theory^{10, 11} (TST), given by

$$r_i = v \cdot \exp\left(-\frac{\Delta E}{k_B T}\right); v = \frac{k_B T q^\ddagger}{h q_0} \quad (2)$$

where $k_B T$ is the product of Boltzmann constant, k_B , and the temperature, T , and ΔE would be the energy barrier for the described transition. In this equation v is the prefactor term obtained from TST with h being the planck constant and q^\ddagger and q_0 , being the partition functions of the transition and initial states, respectively.

The rate of adsorption, r_{ads} , depends on the impingement of adsorbates on the surface. For a non-activated adsorption it can be derived as (3) from equation (2) by inserting the ratio of partition functions for a molecule in the gas phase and in an early 2D transition state,^{10, 12}

$$r_{ads} = \frac{S_0 p_{CO_2} A}{\sqrt{2\pi m k_B T}} \quad (3)$$

where S_0 is the initial sticking coefficient, p_{CO_2} the CO_2 partial pressure above the surface, A the area of an adsorption site, m here the mass of the CO_2 molecule. This equation can also be derived from kinetic gas theory. Commonly, when unknown, initial sticking coefficients are set to unity, assuming a mobile physisorbed precursor state.¹⁰ However, reported initial sticking coefficients were found to be in the range of 0.43-0.73¹³ for CO_2 on clean metal surfaces, which seem more realistic to us. Over the studied temperature range we used the conservative value $S_0 = 0.40$. Equal adsorption probabilities of TopC and MMC 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 —for TiC(001) $A = 1.88 \text{ \AA}^2$; cell parameters reported by Viñes *et al.*⁹—. Adsorption rates have been calculated for *i*) the current atmospheric partial of CO_2 $p_{CO_2} = 40 \text{ Pa}$ ¹⁴, *ii*) for a partial pressure of $p_{CO_2} = 0.15 \text{ bar}$, a benchmark value for postcombustion exhaust gases¹⁵ and *iii*) $p_{CO_2} = 1.0 \text{ bar}$, a partial pressure regime of interest for pure CO_2 stream generation from a CCS system.¹⁶

The rate of desorption, r_{des} , has been obtained from (2) and using the E_{ads} values. Note that by definition E_{ads} is already negative and zero point corrected:

$$r_{des} = v_{des} \cdot \exp\left(\frac{E_{ads}}{k_B T}\right); v_{des} = \frac{k_B T q_{trans,2D}^{gas} q_{rot}^{gas} q_{vib}^{gas}}{h q_{vib}^{ads}} \quad (4)$$

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 $q_{trans,2D}^{gas} q_{rot}^{gas} q_{vib}^{gas}$ in which $q_{trans,2D}^{gas}$ is the partition function for translational motion in two dimensions and q_{rot}^{gas} and q_{vib}^{gas} the rotational and vibrational partition functions in the gas phase. 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

$$q_{trans,2D}^{gas} = A \frac{2\pi m k_B T}{h^2} \quad (5)$$

$$q_{vib}^{ads/gas} = \prod_i \frac{\exp\left(-\frac{h\nu_i}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_B T}\right)} \quad (6)$$

$$q_{rot}^{gas} = T / (T_{rot} 2) \quad (7)$$

where ν_i is the vibrational frequency of each normal mode as obtained from our DFT calculations, either for CO₂ in vacuum or adsorbed. $T_{rot} 2$ 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.¹⁷

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