Electronic Supplementary Information (ESI)

Two-Dimensional Nitrides as Highly Efficient Potential Candidates for CO_2 Capture and Activation

Raul Morales-Salvador, Ángel Morales-García, Francesc Viñes and Francesc Illas*

Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1, 08028 Barcelona, Spain

e-mail: francesc.illas@ub.edu

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1. Interaction of CO_2 with Nitride MXenes

Table S1 compiles the value of the adsorption energy of CO_2 on MXene surfaces along with the C-O and M-O bond lengths, δ(CO) and δ(MO), respectively, the CO_2 molecular angle α(OCO), and the Bader charge difference (ΔQ) between the adsorbed and isolated CO_2 molecule. The information is presented itemized per site as shown in Fig. 1. Note that calculations show a surface-bound anionic $CO_2^{\delta-}$ species with bent geometry (see α(OCO) and ΔQ indicators in Table S1). Several studies have evidenced the key role of this activated mode with the further reaction of CO_2.[1] Previous studies have shown that experimental findings are compatible with the formation of the metastable $CO_2^{\delta-}$ with a bent geometry.[2] The bent anionic structure has larger C-O distances, 1.25-1.44 Å, than the isolated and neutral molecule, 1.16 Å. Our structural analysis reported in Table S1 indicates the formation of $CO_2^{\delta-}$ once the molecule is adsorbed, being consistent with the previous studies.4

Table S1 Adsorption energy (in eV) of CO_2 molecule on MXene carbides at PBE and PBE-D3 levels on the adsorption sites described in Fig. 1. Bond lengths δ(CO) and δ(MO) are given in Å, as well as the CO_2 molecular angle, α(OCO), in degrees. The Bader charge analysis, ΔQ, are given in *e* and corresponds to charge difference between the adsorbed and isolated CO_2 molecule. The (×2) term indicates that the bond distances are identical.

MXene	Level	E_{ads}[a]	δ(MO)	δ(CO)	α(OCO)	ΔQ
			η^1-CO_2-μ^2-C_B			
Cr_2N	PBE	-0.30	2.10 (x 2)	1.26 (×2)	136.8	-0.89
	PBE-D3	-1.30	2.10 (x 2)	1.26 (×2)	136.8	-0.90
Hf_2N	PBE	-2.02	2.18 (x2)	1.29(x2)	130.1	-1.47
	PBE-D3	-2.29	2.18 (x2)	1.29(x2)	129.9	-1.47
Nb_2N	PBE	-1.17	2.24 (×2)	1.27 (×2)	132.6	-1.11
	PBE-D3	-1.73	2.23 (x2)	1.27 (×2)	132.4	-1.12
Ta_2N	PBE	-1.28	2.16 (x2)	1.28 (x2)	132.4	-1.20
	PBE-D3	-1.90	2.16 (x2)	1.28 (x2)	132.4	-1.21
V_2N	PBE	-0.97	2.11 (x2)	1.27 (x2)	134.6	-1.08
	PBE-D3	-1.67	2.10 (x2)	1.27 (x2)	134.6	-1.08
Mo_2N	PBE	-0.74	2.24 (x2)	1.26 (x2)	136.2	-1.06
	PBE-D3	-1.34	2.23 (x2)	1.26 (x2)	136.2	-1.06
W_2N	PBE	-0.40	2.22 (×2)	1.26 (×2)	136,8	-0.86
	PBE-D3	-1.21	2.22 (×2)	1.26 (×2)	136,7	-0.86
			η^2-CO_2-μ^3-C_MO_B			
Nb_2N	PBE	-1.13	2.40 ; 2.39	1.26;1.33	130.8	-1.35
	PBE-D3	-1.69	2.39 (x2)	1.26;1.33	130.9	-1.35
V_2N	PBE	-0.94	2.25;2.24	1.26;1.32	133.1	-1.30
	PBE-D3	-1.65	2.23;2.25	1.26;1.32	133.1	-1.30
Mo_2N	PB3	-0.44	2.36;2.36	1.26;1.30	134.7	-1.39
	PB3-D3	-1.03	2.35;.23.6	1.26;1.30	134.7	-1.39
			η^2-CO_2-μ^3-C_NO_B			
Cr_2N	PBE	-0.21	2.22;2.18	1.25;1.31	135.0	-1.12
	PBE-D3	-1.21	2.22;2.17	1.25;1.31	135.0	-1.14

Nb_2N	PBE	-0.93	2.39;2.36	1.26;1.33	132.1	-1.34
	PBE-D3	-1.50	2.39;2.36	1.26;1.33	132.2	-1.35
V_2N	PBE	-0.80	2.26;2.21	1.26;1.32	133.9	-1.32
	PBE-D3	-1.51	2.25;2.21	1.26;1.33	134.0	-1.32
η^3-CO_2-μ^5-$C_MO_NO_N$						
Zr_2N	PBE	-2.62	2.34 ; 2.35	1.36 (x2)	116.2	-1.79
	PBE-D3	-2.97	2.34 ; 2.35	1.36;1.37	116.2	-1.80
Hf_2N	PBE	-2.68	2.32 ; 2.33	1.35;1.44	114.0	-2.02
	PBE-D3	-2.97	2.22;2.33	1.35;1.44	114.0	-2.02
Ti_2N	PBE	-2.62	2.23 (x2)	1.40;1.36	115.9	-1.86
	PBE-D3	-3.13	2.23;2.19	1.40;1.36	115.9	-1.87
η^3-CO_2-μ^5-$C_NO_MO_M$						
Ta_2N	PBE	-1.26	2.00(x2)	1.38 (x2)	112.8	-1.65
	PBE-D3	-1.90	2.00(x2)	1.38 (x2)	112.8	-1.65
W_2N	PBE	-0.94	2.00 (x2)	1.37 (x2)	114.0	-1.40
	PBE-D3	-1.77	2.00 (x2)	1.37 (x2)	114.0	-1.40
Ti_2N	PBE	-2.62	2.20;2.14(x2)	1.39;1.40	115.3	-1.94
	PBE-D3	-3.13	2.20;2.13(x2)	1.39;1.40	115.2	-1.94
η^2-CO_2-μ^4-O_BO_B						
Ta_2N	PBE	+0.05	2.10;2.30(x2)	1.39 (x2)	106.8	-1.62
	PBE-D3	-0.61	2.10;2.31	1.39 (x2)	106.8	-1.63
η^3-CO_2-μ^4-$C_BO_BO_B$						
Mo_2N	PBE	-0.74	2.22;2.28	1.38;1.36	111.2	-1.81
	PBE-D3	-1.34	2.22;2.28	1.38;1.36	111.2	-1.82
Cr_2N	PBE	-0.41	2.09;1.98	1.39;1.29	121.31	-1.27
	PBE-D3	-1.44	2.08;1.97	1.39;1.29	121.33	-1.28
η^3-CO_2-μ^4-$C_MO_MO_B$						
W_2N	PBE	-1.84	2.17;2.04	1.33;1.39	116.5	-1.41
	PBE-D3	-2.59	2.17;2.04	1.33;1.39	116.5	-1.41

[a] ZPE corrected as above stated.

2. Effect of Dispersion in the Adsorption of CO_2 on Nitride MXenes

The contribution of dispersion terms becomes significant once the D3 Grimme method is turned on when evaluating the adsorption energy on nitride MXenes. The adsorption energy (E_{ads}) strengthens by 0.7–1.00 eV. Other corrections such as Tkatchenko-Scheffler (TS) and sophisticated surface (*surf*) many-body dispersion energy (MBD) confirm that the effect of dispersion is quite important when MXene nitrides are used as substrates. Table S2 show a detail analysis of the dispersion contribution on T_2N and V_2N.

Table S2 E_{ads} of CO_2 on Ti_2N and V_2N by using D3, Tkatchenko-Scheffler (TS), and many-body dispersion energy (MBD) methods. Note that ZPE contribution is also considered.

	PBE	**PBE-D3**	**PBE-TS**	**PBE-MBD**
Ti_2N	-2.62	-3.12	-3.02	-3.25
V_2N	-0.97	-1.66	-1.68	-1.66

3. Adsorption/Desorption Temperatures

This adsorption/desorption rate model allows one to calculate the rates for desorption and adsorption of CO_2 on MXene (0001) surfaces. Table S3 reports the range of desorption temperature for each one of the adsorption sites studied (see Fig. 1). The reported temperature range is interpreted as the range in which MXene surface loses its capacity to initially capture and accumulate CO_2 when annealing.

Table S3 Desorption temperature range ([PBE]–[PBE-D3]) for CO_2 partial pressure ranges for CO_2 partial pressures of 40, $15 \cdot 10^3$, and 10^5 Pa, which stand for air, exhaust, and desorption situations, respectively. All temperature values are given in K.

MXene	Temperature range		
	air	**exhaust**	**desorption**
η^1-CO_2-μ^2-C_B			
Cr_2N	137-548	171-704	186-776
Hf_2N	884-1004	1153-1316	1280-1463
Nb_2N	500-741	644-958	710-1060
Ta_2N	524-784	666-1004	729-1104
V_2N	416-715	532-924	585-1023
Mo_2N	315-559	398-718	436-791
W_2N	171-498	213-634	232-696
η^2-CO_2-μ^3-C_MO_B			
Nb_2N	500-749	647-979	716-1086
V_2N	420-730	541-952	597-1057
Mo_2N	203-453	259-586	285-648
η^2-CO_2-μ^3-C_NO_B			
Cr_2N	106-523	135-672	145-741
Nb_2N	409-650	525-843	577-934
V_2N	354-661	454-859	499-949
η^3-CO_2-μ^5-$C_MO_NO_N$			
Zr_2N	1148-1256	1482-1625	1636-1796
Hf_2N	1172-1261	1492-1631	1637-1804
Ti_2N	1108-1326	1430-1716	1579-1897
η^3-CO_2-μ^5-$C_NO_MO_M$			
Ta_2N	507-761	638-962	694-1053
W_2N	374-697	466-877	504-956
Ti_2N	1114-1339	1441-1736	1594-1922
η^2-CO_2-μ^4-O_BO_B			
Ta_2N[a]	276	344	377
η^3-CO_2-μ^4-$C_BO_BO_B$			
Mo_2N	313-531	394-669	431-729
Cr_2N	181-579	225-734	242-803
η^3-CO_2-μ^4-$C_MO_MO_B$			
W_2N	728-1029	919-1305	1000-1430

[a] Adsorption energy at PBE gives positive values, hence only PBE-D3 temperatures are given

4. Quantitative Adsorption of CO_2 by Nitride MXenes

The effectiveness of the nitride MXene materials is also investigated to quantify the amount of CO_2 adsorbed per MXene amount as mol CO_2/kg of material, and compared with their carbide counterparts. For this purpose, we assumed that four CO_2 molecules could be simultaneously adsorbed on each one of the MXene surfaces within the employed (3×3) supercell, giving a total of 8 adsorbed CO_2 molecules (upper and bottom layers covered by CO_2). Table S4 encompasses the estimated CO_2 uptake for the nitride MXene surfaces considered in the present work along with previous computational results for several carbide MXenes,[3] experimental evidences of zeolites, metal-organic-frameworks (MOFs), active carbons, and graphene and derivatives.[4]

Table S4. Comparison of CO_2 adsorption capacity of MXene carbides and nitrides with other solid adsorbents: zeolites, MOFs, MgO nanopowders,[5] graphene and graphene derivatives (further details in Ref. 12 and references therein).

Material	**CO_2 uptake** (mol CO_2/kg. substrate)	
	Nitrides (*X*=N)	Carbides (*X*=C)
MXene		
Ti_2X	7.96	8.25
V_2X	7.56	7.80
Cr_2X	7.41	-
Zr_2X	4.48	4.57
Nb_2X	4.40	4.49
Mo_2X	4.27	4.36
Hf_2X	2.38	2.41
Ta_2X	2.35	2.37
W_2X	2.32	2.34
Zeolites		
Ca-X	3.36	
13X	3.96	
MOFs		
Cu-BTTri-mmen	2.38	
MgO nanopowders	0.92	
Graphene & derivatives		
a-RGO-750	2.18	
a-RGO-850	2.75	

a-RGO-950	3.36

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