Tuning Transition Metal Carbides Activity by Surface Metal Alloying: Case Study on CO_2 Capture and Activation

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Table S1 Bader charges of all bare surfaces. q^{sur} is the computed charge of surface carbons directly bound to the dopant. q^{sub} is the computed charge on subsurface carbon. q^{TM} is the computed charge of the doping transition metal atom. All values are given in *e*.

Bare Surfaces			
Dopant	q^{sur}	q^{sub}	q^{TM}
Ti	-1.70	-1.81	-
Cr	-1.58	-1.64	+1.31
Hf	-1.74	-1.90	+2.03
Mo	-1.59	-1.61	+1.41
Nb	-1.66	-1.76	+1.72
Ta	-1.70	-1.81	+1.91
V	-1.64	-1.73	+1.56
W	-1.63	-1.72	+1.69
Zr	-1.68	-1.85	+1.78

Table S2 Binding modes, and adsorption energies (E_{ads}) with and without van der Waals corrections (vdW), as obtained PBE-D3, as well as geometry parameters, including CO_2 angle, C-C bond distances, *d*(C-C), and CO_2 molecule C-O bond distances, *d*(C-O).

CO_2 Adsorption						
Dopant	Binding Mode	E_{ads} (eV)	E_{ads} vdW (eV)	CO_2 angle (º)	d(C-C) (Å)	d(C-O) (Å)
Ti	TopC	-0.61	-0.87	127.5	1.48	1.29
	TopC-adj					
	MMC	-0.63	-0.89	122.5	1.49	1.30
Cr	TopC	-0.18	-0.47	126.2	1.51	1.25,1.32
	TopC-adj	-0.62	-0.90	128.0	1.49	1.28
	MMC	-0.23	-0.55	122.5	1.49	1.30,1.29
Hf	TopC	-0.96	-1.20	126.0	1.49	1.28,1.30
	TopC-adj	-0.56	-0.81	126.9	1.48	1.29
	MMC	-0.81	-1.06	122.1	1.50	1.29,1.30
Mo	TopC	-0.18	-0.45	127.8	1.49	1.29,1.28
	TopC-adj	-0.39	-0.67	128.4	1.50	1.28
	MMC	-0.13	-0.42	122.8	1.50	1.29
Nb	TopC	-0.50	-0.76	127.0	1.49	1.28,1.29
	TopC-adj	-0.40	-0.67	127.8	1.49	1.29
	MMC	-0.42	-0.68	122.4	1.50	1.29,1.30
Ta	TopC	-0.57	-0.83	127.1	1.49	1.28,1.30
	TopC-adj	-0.36	-0.61	128.0	1.50	1.29
	MMC	-0.52	-0.78	122.1	1.50	1.29,1.30
V	TopC	-0.28	-0.55	128.2	1.48	1.29,1.28
	TopC-adj	-0.57	-0.82	127.9	1.49	1.29
	MMC	-0.36	-0.63	122.6	1.49	1.30,1.29
W	TopC	-0.22	-0.48	128.0	1.48	1.28,1.29
	TopC-adj	-0.31	-0.57	128.6	1.50	1.28
	MMC	-0.18	-0.45	122.4	1.50	1.29,1.30
Zr	TopC	-0.93	-1.17	125.7	1.50	1.28,1.30
	TopC-adj	-0.61	-0.86	126.5	1.47	1.29
	MMC	-0.74	-0.98	122.3	1.50	1.29,1.30

Table S3 Bader charges for all the studied surfaces with adsorbed CO_2 Here q^{C-C} is the Bader charge of the surface C atom involved in the CO_2 adsorption.

CO_2 adsorbed						
Dopant	Binding Mode	q^{surf}	q^{C-C}	q^{sub}	q^{TM}	q^{CO_2}
Ti	TopC TopC-adj	-1.67	-1.40	-1.81	-	-0.82
	MMC	-1.65	-1.33	-1.83	+1.81	-0.86
Cr	TopC	-1.54	-1.33	-1.64	+1.35	-0.76
	TopC-adj	-1.54	-1.34	-1.61	+1.29	-0.78
	MMC	-1.48	-1.27	-1.69	+1.35	-0.81
Hf	TopC	-1.73	-1.32	-1.87	+2.18	-0.97
	TopC-adj	-1.73	-1.40	-1.88	+2.01	-0.88
	MMC	-1.72	-1.37	-1.88	+2.16	-0.90
Mo	TopC	-1.56	-1.31	-1.65	+1.55	-0.83
	TopC-adj	-1.55	-1.30	-1.58	+1.38	-0.85
	MMC	-1.53	-1.29	-1.69	+1.53	-0.82
Nb	TopC	-1.65	-1.32	-1.79	+1.88	-0.87
	TopC-adj	-1.64	-1.35	-1.74	+1.73	-0.87
	MMC	-1.62	-1.32	-1.81	+1.84	-0.85
Ta	TopC	-1.69	-1.35	-1.84	+2.12	-0.88
	TopC-adj	-1.68	-1.35	-1.78	+1.93	-0.89
	MMC	-1.68	-1.34	-1.86	+2.11	-0.88
V	TopC	-1.60	-1.20	-1.75	+1.64	-0.95
	TopC-adj	-1.61	-1.37	-1.73	+1.57	-0.80
	MMC	-1.57	-1.30	-1.79	+1.65	-0.83
W	TopC	-1.60	-1.34	-1.68	+1.76	-0.82
	TopC-adj	-1.60	-1.31	-1.62	+1.60	-0.85
	MMC	-1.57	-1.31	-1.74	+1.76	-0.84
Zr	TopC	-1.69	-1.27	-1.83	+1.98	-0.98
	TopC-adj	-1.67	-1.27	-1.84	+1.86	-0.98
	MMC	-1.68	-1.34	-1.84	+1.97	-0.88

Fig. S1 Top view of the (3√2×3√2)R45º model, the CO_2 was adsorbed both in the shown position but the dopant was moved from Near to Far position. The carbon from the CO_2 is represented in light brown to contrast the carbons from the slab (dark brown).

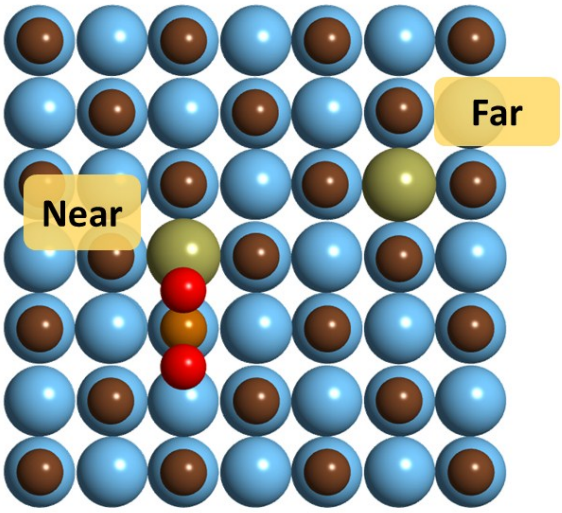

Fig. S2 Top view of the slab model used to represent a higher coverage situation. Note that due to periodic symmetry, the CO_2 adsorbed at the four corners correspond to the same molecule.