Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

How bulk and surface properties of Ti_4SiC_3, V_4SiC_3, Nb_4SiC_3 and Zr_4SiC_3 tune reactivity: A computational study

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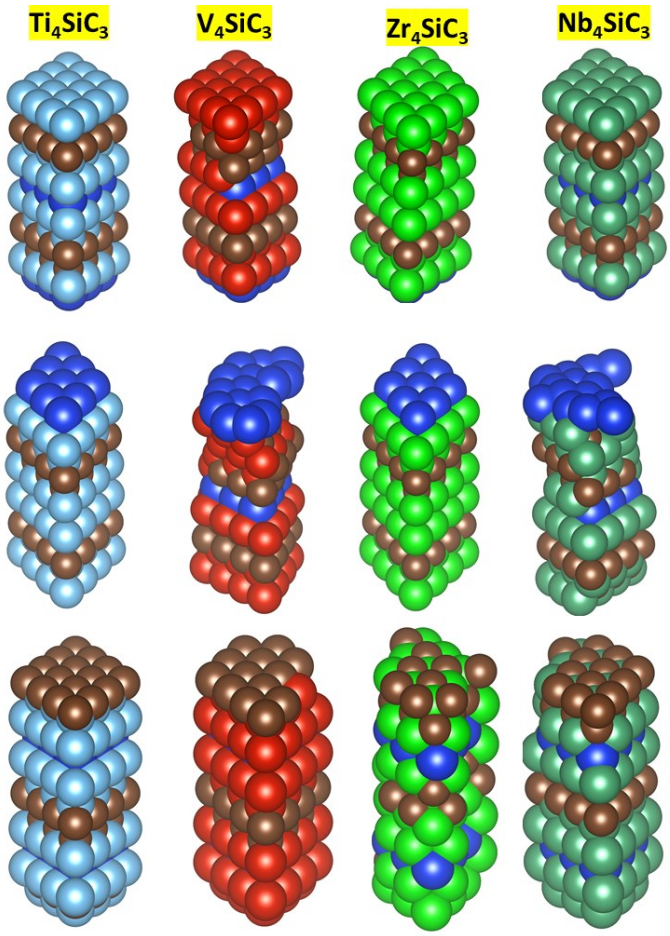

Figure S1. Negative correlation between chemical adsorption energy and the imaginary frequency for the CO_2 reduction transition state.

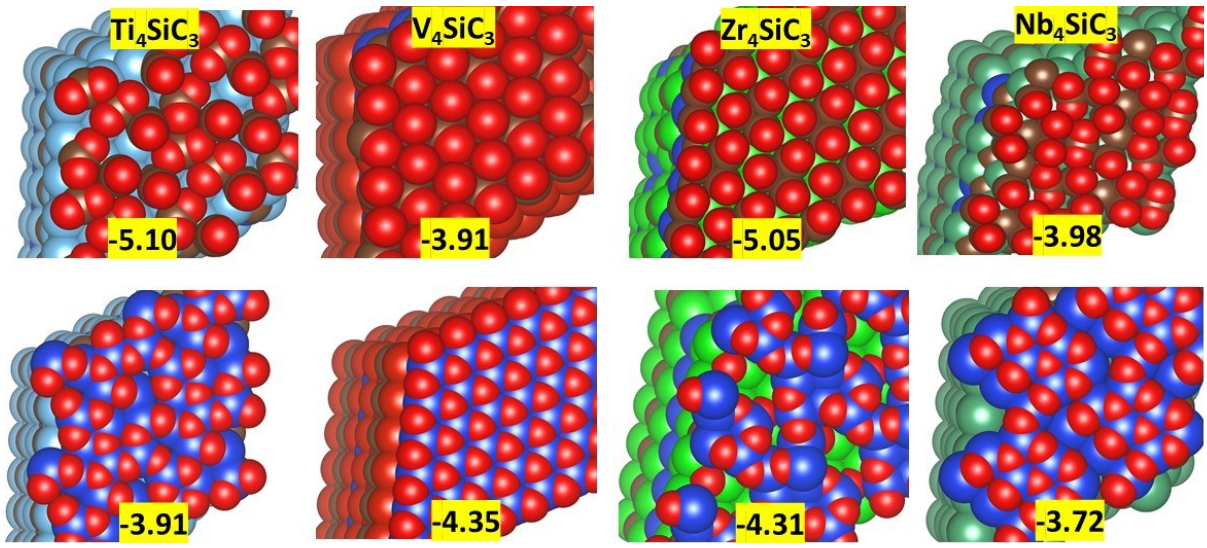

Figure S2. Oxygen monolayers morphology on top of the carbon (top) and silicon terminations of the MAX-phase silicon carbides. Eight oxygen atoms were added to each surface and all adsorption energies are given per oxygen atom relative to the relaxed surfaces and molecular triplet O_2.

Table S3. Energies for geometry scan of molecular hydrogen from the vacuum to the surfaces of four MAX-phase silicon carbides. All energies are given in eV relative to the physically adsorbed species.

	Ti_4SiC_3	V_4SiC_3	Zr_4SiC_3	Nb_4SiC_3
[a]**Ads**	-0.03	-0.03	-0.03	-0.04
Scan 01	0.00	0.00	0.00	0.00
Scan 02	0.01	0.01	0.01	0.01
Scan 03	0.01	0.01	0.01	0.01
Scan 04	0.01	0.01	0.01	0.00
Scan 05	0.01	0.01	0.00	0.00
Scan 06	0.00	0.01	-0.02	0.00
Scan 07	0.00	0.01	-0.03	0.00
Scan 08	-0.01	0.00	-0.04	-0.01
Scan 09	-0.04	0.00	-0.05	-0.02
Scan 10	-0.05	-0.03	-0.08	-0.02
Scan 11	-0.06	-0.04	-0.11	-0.04
Scan 12	-0.08	-0.05	-0.18	-0.16
Scan 13	-0.11	-0.07	-0.27	-0.34
Scan 14	-0.16	-0.07	-0.31	-0.58
Scan 15	-0.27	-0.13		-0.73
Scan 16	-0.44	-0.24		-0.66
Scan 17		-0.47		-2.15
Scan 18		-0.75		
Scan 19		-0.89		
[b]**Ads**	-2.53	-1.96	-2.27	-2.18

[a]**Ads** physically adsorbed H_2. [b]**Ads** chemically adsorbed H_2.

Table S4. Energies for geometry scan of molecular carbon dioxide from the vacuum to the surfaces of three MAX-phase silicon carbides. No physically adsorbed mode could be obtained for CO_2 on Ti_4SiC_3. All energies are given in eV relative to the physically adsorbed species.

	V_4SiC_3	Zr_4SiC_3	Nb_4SiC_3
[a]**Ads**	-0.24	-0.36	-0.17
Scan 01	0.05	0.28	0.06
Scan 02	0.07	0.29	0.08
Scan 03	0.08	0.29	0.11
Scan 04	0.08	0.30	0.11
Scan 05	0.09	0.30	0.10
Scan 06	0.08	0.30	0.09
Scan 07	0.07	0.29	0.07
Scan 08	0.06	0.28	0.04
Scan 09	0.04	0.25	0.01
Scan 10	0.02	0.23	-0.09
Scan 11	-0.01	0.13	-0.15
Scan 12	-0.04	-0.18	-0.25
Scan 13	-0.06	-0.32	-0.42
Scan 14	-0.10		-1.04
Scan 15	-0.21		
Scan 16	-0.25		
Scan 17	-0.38		
Scan 18	-0.85		
Scan 19	-1.50		
[b]**Ads**	-1.76	-3.25	-1.72

[a]**Ads** physically adsorbed CO_2. [b]**Ads** chemically adsorbed CO_2.

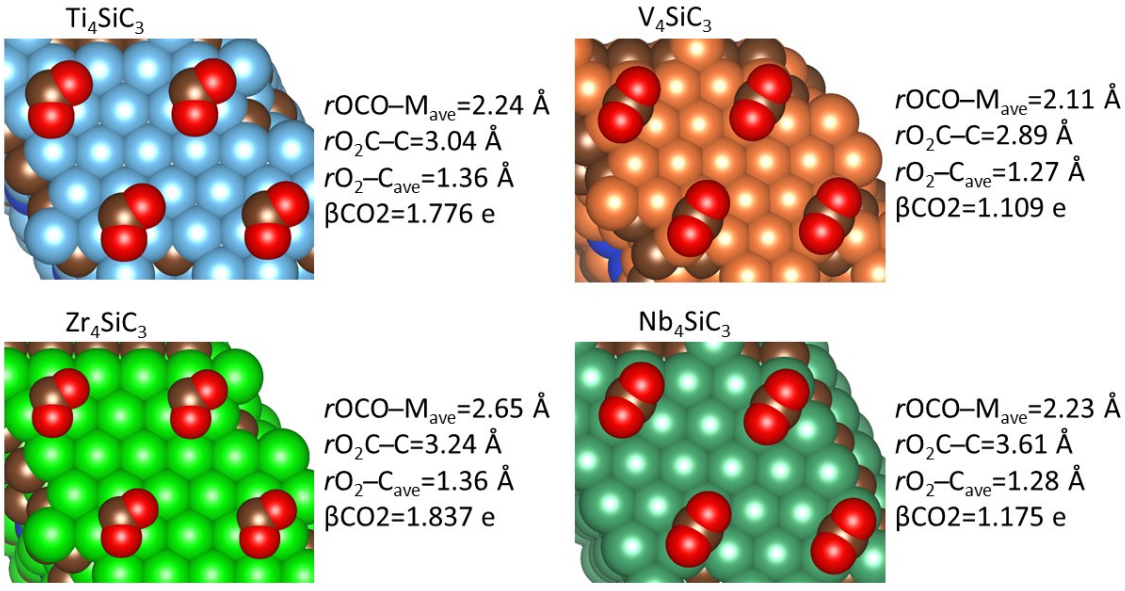

Figure S5. Adsorption of CO2 on top of the metal terminated (0001) basal plane of the four silicon carbides under study. Important, bond distances are given in angstroms, whilst bader charge transfer is grouped to the CO2 adsorbate.