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Supporting Information

The Role of Vacancies in a Ti_2CT_x MXene-Derived Catalyst for Butane Oxidative Dehydrogenation

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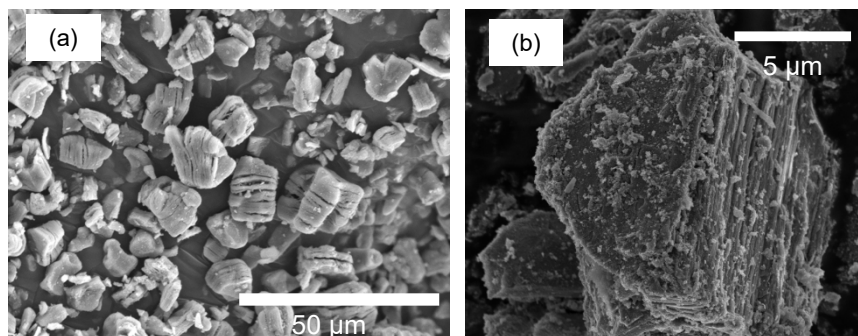


Figure S1. SEM images of a) fresh Ti_2CT_x and b) Ti_2CT_x after ODH stability test at 500 °C.

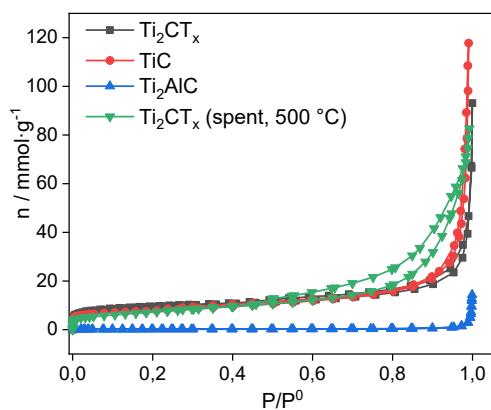


Figure S2. Nitrogen adsorption-desorption isotherms at 77 K of the studied catalysts.

Table S1. BET surface area (S_{BET}) and total pore volume (V_t) of the studied catalysts.

Catalyst	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_t ($\text{cm}^3\cdot\text{g}^{-1}$)
Ti_2CT_x	33	0.07
TiC (commercial)	27	0.17
Ti_2AlC	1	0.01
Ti_2CT_x (spent, 500 °C)	26	0.12
TiO_2 (anatase)	316	0.57
TiO_2 (A+R)	20	0.15

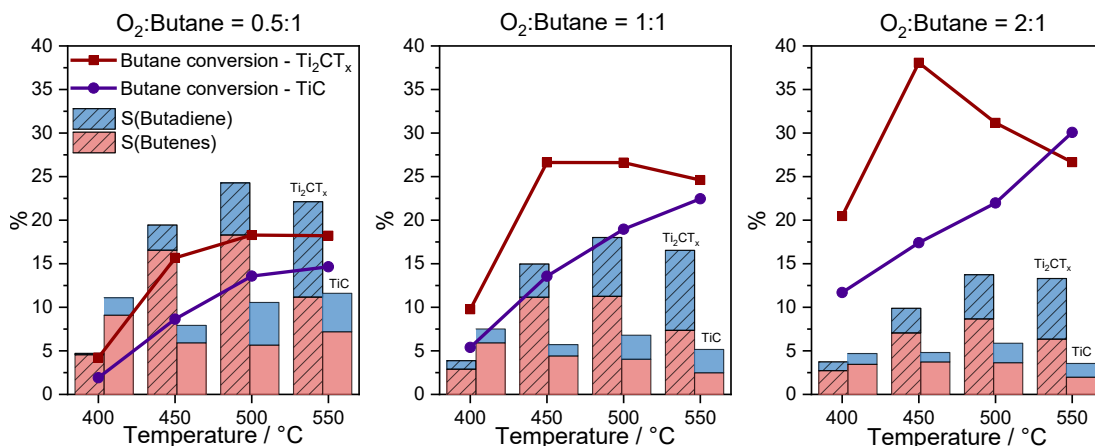


Figure S3. Catalytic performance of Ti_2CT_x and commercial TiC during temperature screening tests. a) O_2 /butane = 0.5:1, b) O_2 /butane = 1:1, c) O_2 /butane = 2:1. Reaction conditions: 300 mg catalyst, total flow $30\text{ mL}\cdot\text{min}^{-1}$, atmospheric pressure.

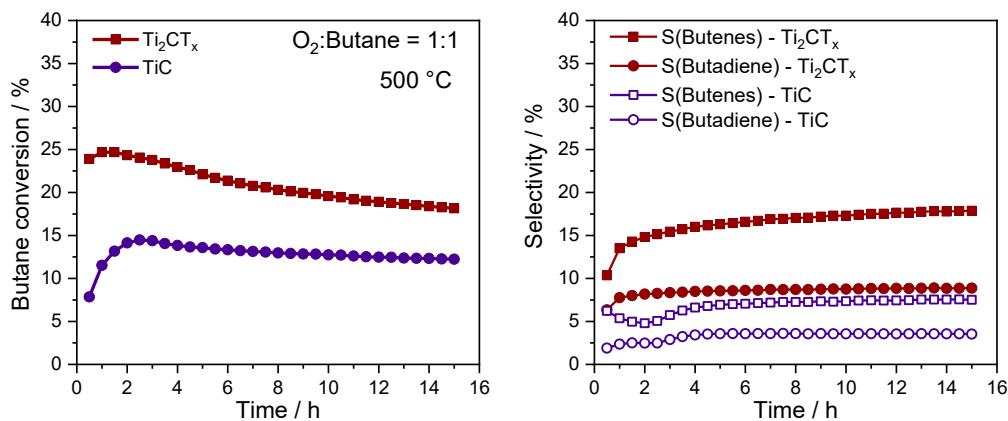


Figure S4. Catalytic performance of Ti_2CT_x and commercial TiC during stability tests at $500\text{ }^\circ\text{C}$. Reaction conditions: O_2 /butane = 1:1, 300 mg catalyst, total flow $30\text{ mL}\cdot\text{min}^{-1}$, atmospheric pressure.

Table S2. Elemental atomic percentage on the surface of the catalysts and the Ti 2p intensity ratios between oxide and carbide, obtained from XPS analysis.

Catalyst	Atom fraction (%) on the surface				
	Ti	Al	O	C	F
Ti_2CT_x	0.6	-	1.5	97.8	0.1
Ti_2AlC	6.1	18.3	52.9	22.6	-
TiC (commercial)	0.4	-	0.5	99.1	-
TiO_2 (anatase)	16.2	-	43.4	40.4	-
TiO_2 (rutile)	21.8	-	52.7	25.5	-
TiO_2 (A+R)	23.4	-	55.0	21.6	-
Ti_2CT_x (spent, $500\text{ }^\circ\text{C}$)	1.1	-	2.7	96.2	0

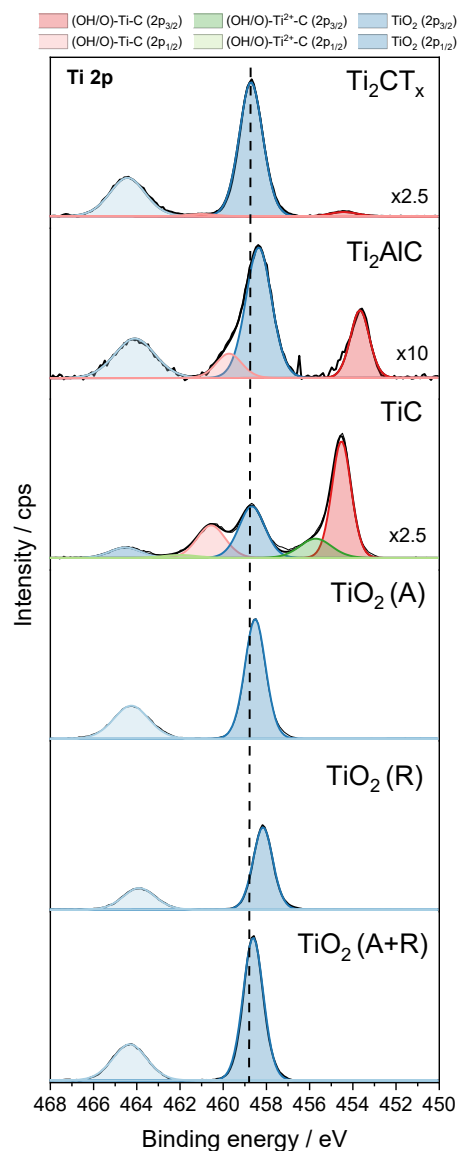


Figure S5. Ti 2p XPS spectra of the studied catalysts. Compared to the TiO_2 references, the TiO_2 peak position in the Ti_2CT_x MXene is closer to the anatase and rutile mixture (458.6 eV), indicating that the oxide layer is a mixture of these two phases.

Please note that the deconvolution of XP spectra is complicated and multiple splitting due to L-S coupling must be taken into account. The case of Ti 2p core level is especially complicated, since the splitting value varies with the chemical state. As an example, we can say that TiC or TiN has a $2p_{1/2}$ - $2p_{3/2}$ splitting of 6 eV. TiO_2 has a splitting of 5.7 eV.[1,2] The good resolution of the collected spectra allows us to differentiate the species (TiC or TiO_2). Thus, we have deconvoluted the spectra without putting any restrictions. Once deconvoluted, we verified that the splitting is within the expected values and corresponds to what we find in the literature. As an example, we can use the Ti_2AlC sample above. Here we can see that the separation between the peaks shaded in red is 6 eV, which

corresponds to TiC, while the separation between the peaks shaded in blue is 5.7 eV, corresponding to TiO₂.

This was done for all the samples, and in all of them it was verified that the gave us multiple splitting results between 5.7 and 6 eV. In all the samples, the splitting was around 6 eV when it came to TiC and and around 5.7 eV when it came to TiO₂.

1. Peng, W.-C.; Chen, Y.-C.; He, J.-L.; Ou, S.-L.; Horng, R.-H.; Wu, D.-S. Tunability of p- and n-channel TiOx thin film transistors. *Sci. Rep.* 2018, 8, 9255, doi:10.1038/s41598-018-27598-5.
2. Ignaszak, A.; Song, C.; Zhu, W.; Zhang, J.; Bauer, A.; Baker, R.; Neburchilov, V.; Ye, S.; Campbell, S. Titanium carbide and its core-shelled derivative TiC@TiO₂ as catalyst supports for proton exchange membrane fuel cells. *Electrochim. Acta* 2012, 69, 397–405, doi:https://doi.org/10.1016/j.electacta.2012.03.039.

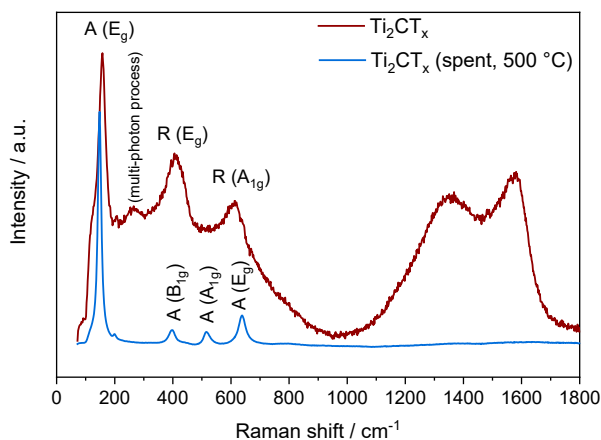


Figure S6. Raman spectra of fresh Ti₂CT_x and spent Ti₂CT_x (after ODH stability test at 500 °C). The spectra of the fresh sample shows the presence of disordered graphite at 1349 cm⁻¹ (D band) and 1583 cm⁻¹ (G band).

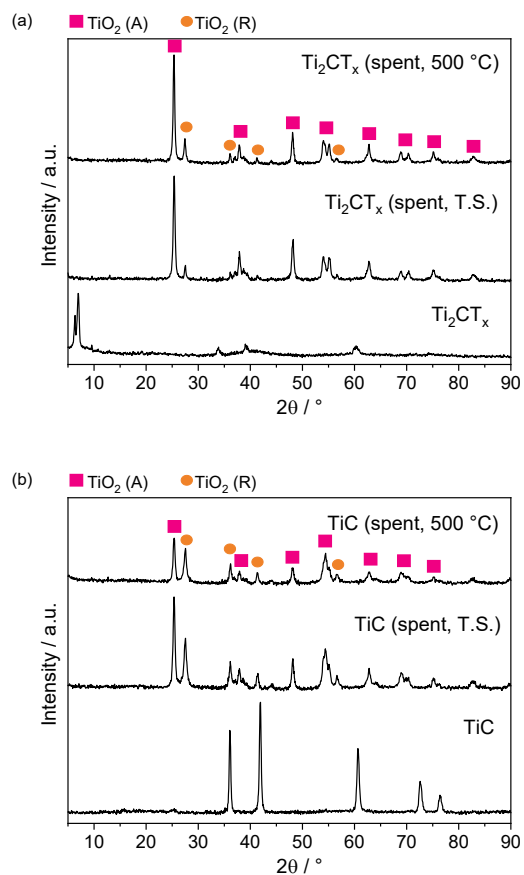


Figure S7. XRD patterns of Ti_2CT_x and commercial TiC catalysts fresh, after temperature screening reaction (spent, T.S.) and after stability tests at 500 °C (spent, 500 °C).

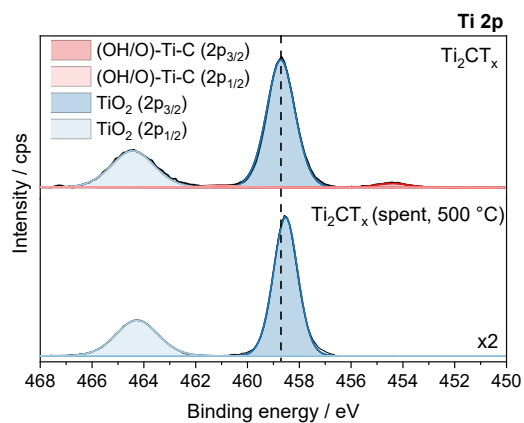


Figure S8. Ti 2p XPS spectra of fresh and spent Ti_2CT_x catalyst.

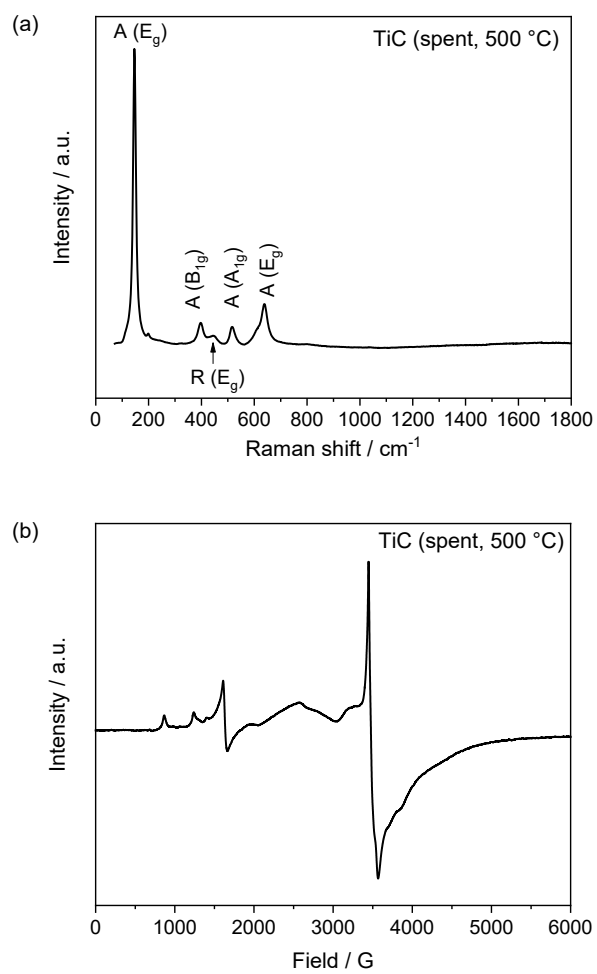


Figure S9. a) Raman spectrum and b) experimental EPR spectrum of the spent commercial TiC catalyst.

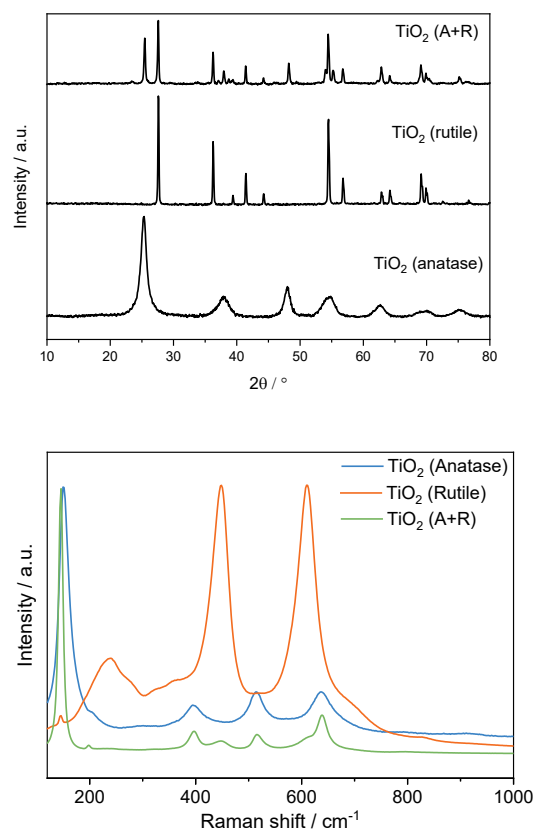
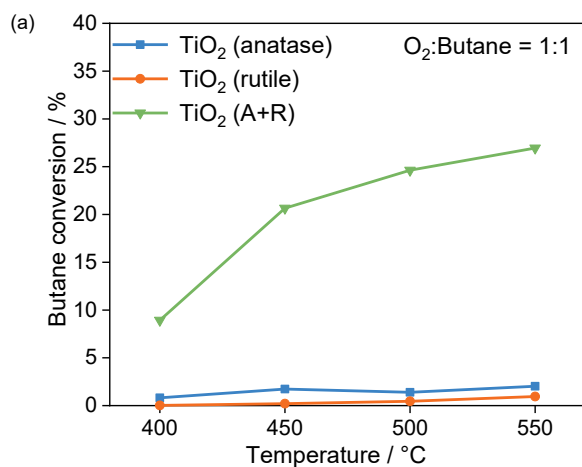


Figure S10. Top: XRD patterns of anatase TiO₂, rutile TiO₂, and a mixture of anatase and rutile TiO₂. From the intensity of the anatase peak at $2\theta = 24.4^\circ$ and the rutile peak at $2\theta = 27.6^\circ$, we estimate that the TiO₂ (A+R) sample contains 44% of anatase phase and 56% of rutile phase. Bottom: Raman spectra of the TiO₂ materials.



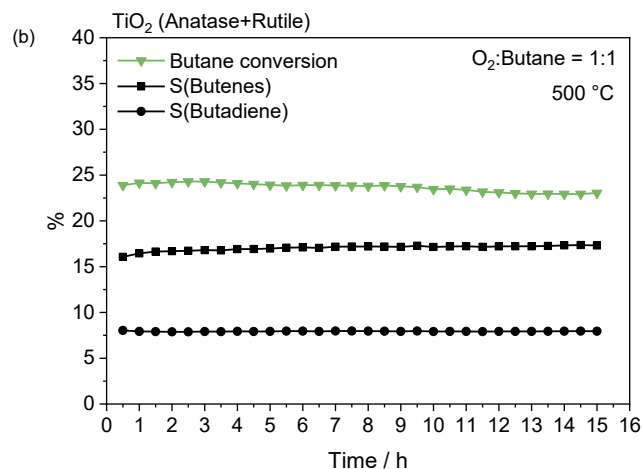


Figure S11. a) Butane conversion values of the TiO₂ materials during temperature screening at an O₂/butane = 1:1, b) Catalytic performance of TiO₂ (Anatase+Rutile) during the stability test at 500 °C and at an O₂/butane = 1:1. All the catalytic tests were performed using 300 mg of catalyst and a total flow of 30 mL·min⁻¹.

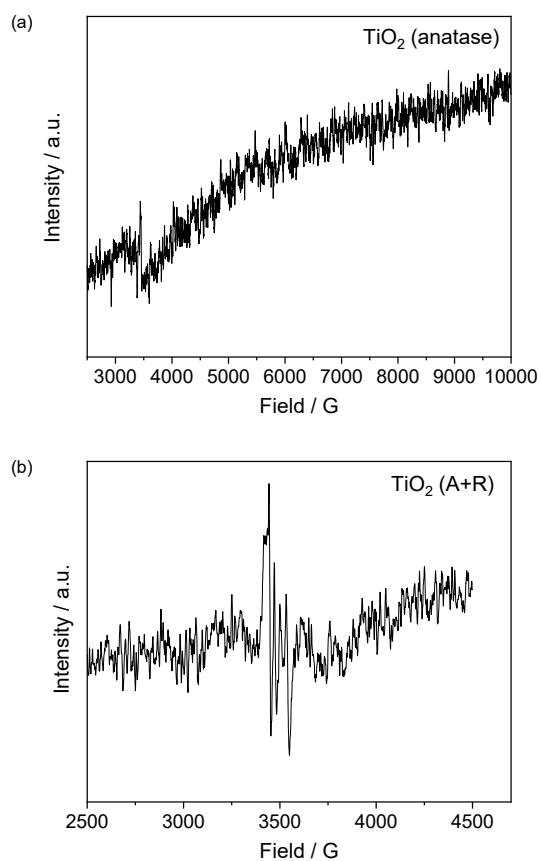


Figure S12. EPR (measured at 10 K) spectra of a) anatase TiO₂ (experimental parameters: microwave frequency 9.647415 GHz, power 0.6325 mW, modulation amplitude 4.000 G) and b) TiO₂ (A+R) (experimental parameters: microwave frequency 9.649052 GHz, power 0.6325 mW, modulation amplitude 4.000 G).