

## Electronic Supplementary Information

### Transformation of Titanium Carbide into Mesoporous Titania for Catalysed HBr Oxidation

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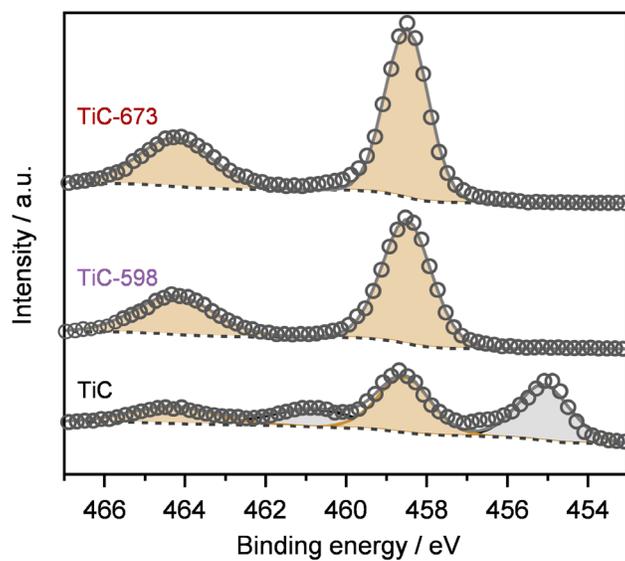
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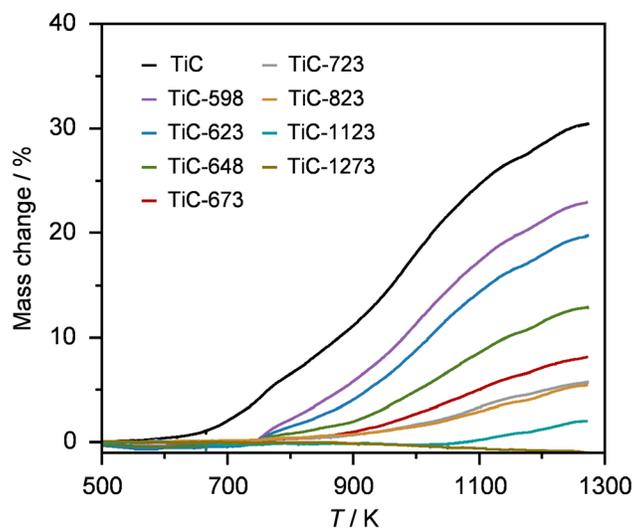
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**Table S1.** Surface composition determined by X-ray photoelectron spectroscopy of TiC in fresh form and after thermal treatment in air at 598-823 K.

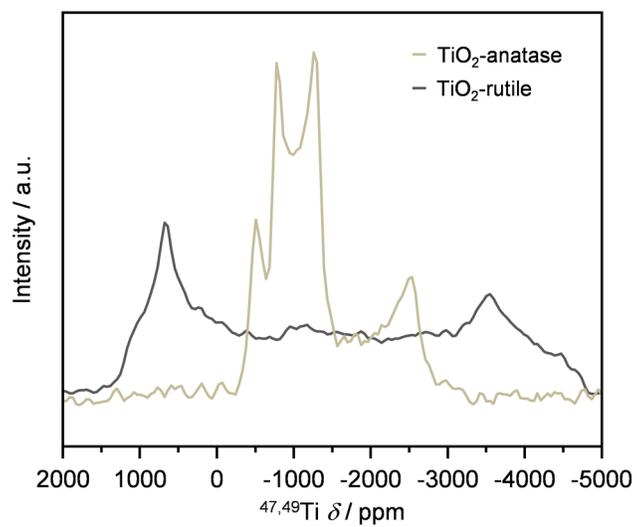
Sample	Ti content / at.%	O content / at.%	C content / at.%	O:Ti / -	C:Ti / -
TiC	20.4	35.4	44.2	1.72	2.17
TiC-598	22.4	51.9	25.7	2.32	1.15
TiC-623	25.5	56.4	18.1	2.22	0.71
TiC-648	26.3	57.7	16.0	2.17	0.61
TiC-673	26.7	59.0	14.3	2.22	0.53
TiC-723	26.3	58.6	15.1	2.22	0.57
TiC-823	25.7	59.6	14.7	2.22	0.57



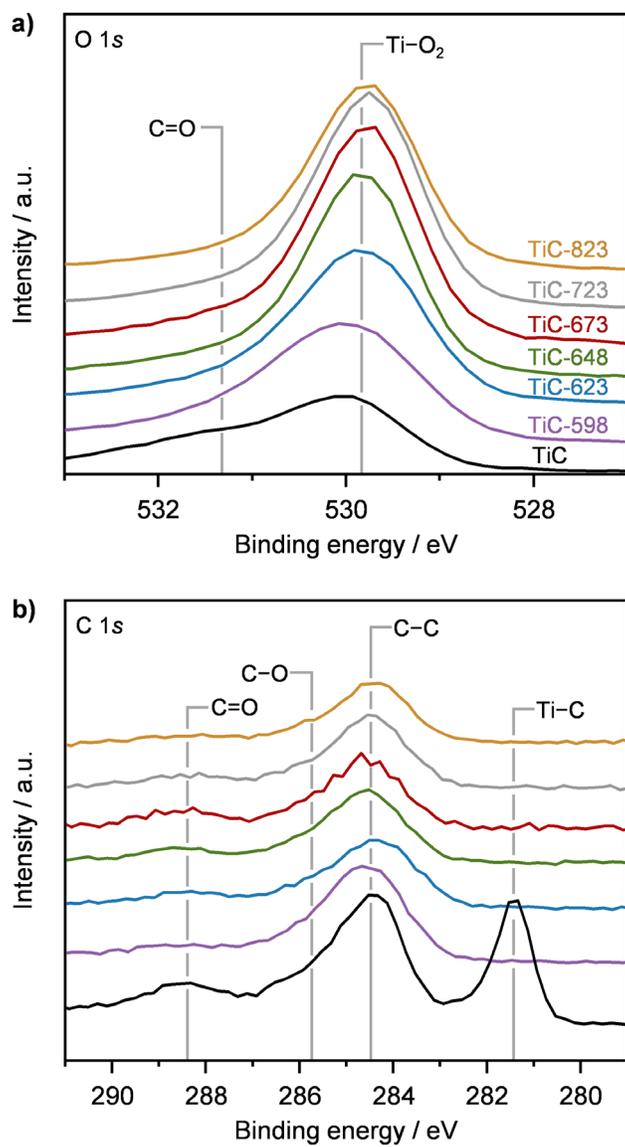
**Fig. S1** Ti 2*p* core level spectra of fresh TiC and thermally treated at 598 K and 673 K. The solid lines and open circles represent the overall fit and the raw data, respectively. The orange- and gray-colored areas denote TiO<sub>2</sub> and TiC, respectively.



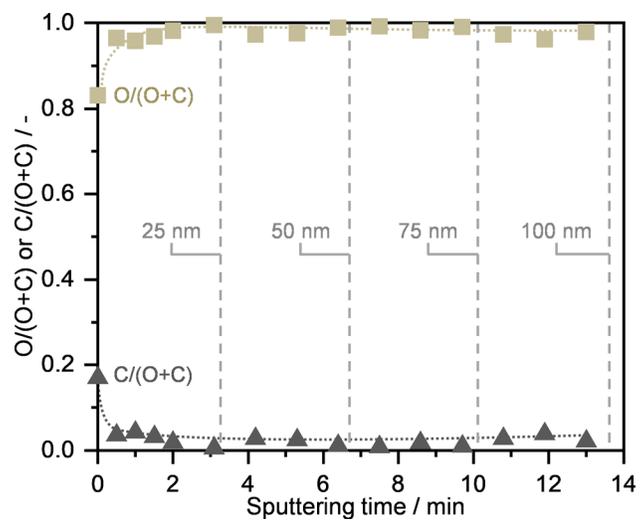
**Fig. S2** Thermogravimetric analysis of TiC in fresh form and after thermal treatment in air at different temperatures. Quantification of the remaining TiC was assessed by integrating the profiles in the full temperature window investigated. The results are shown in **Figure 1** of the main manuscript.



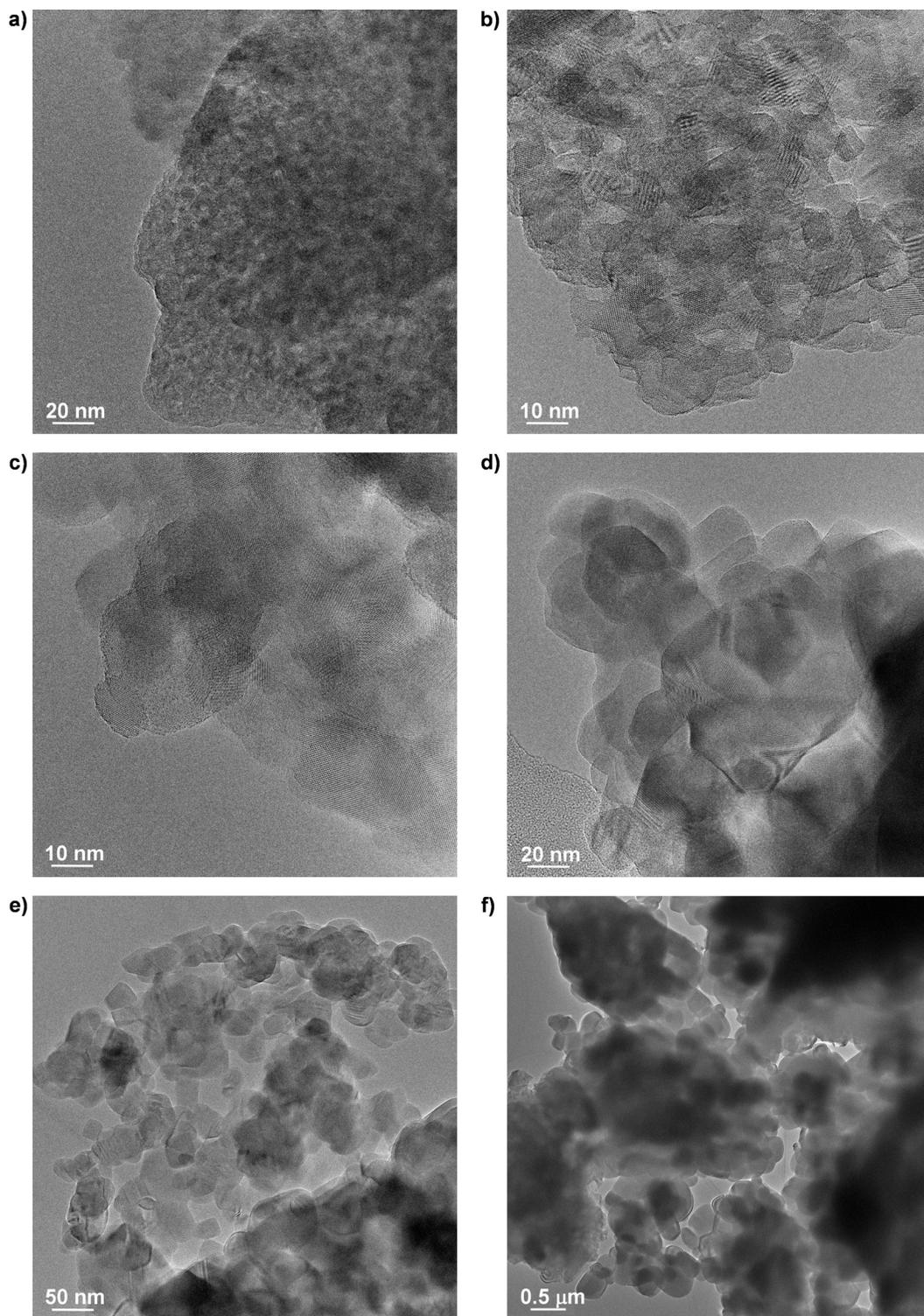
**Fig. S3**  $^{47,49}\text{Ti}$  nuclear magnetic resonance spectroscopy of commercial  $\text{TiO}_2$ -anatase and  $\text{TiO}_2$ -rutile.



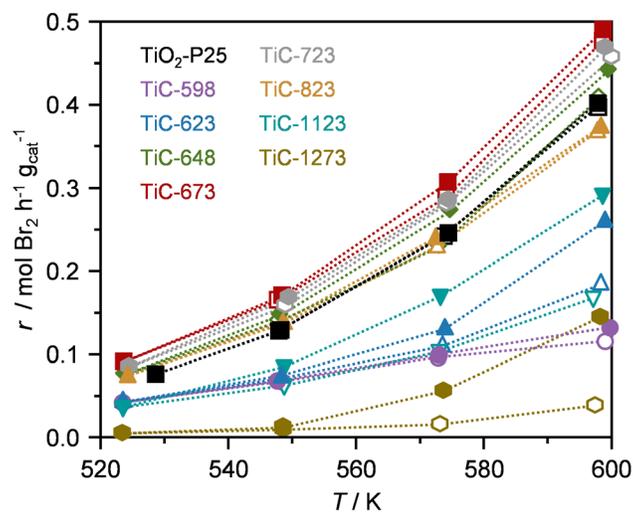
**Fig. S4** a) C 1s and b) O 1s core-level X-ray photoelectron spectra of TiC in fresh form and after thermal treatment in air at different temperatures.



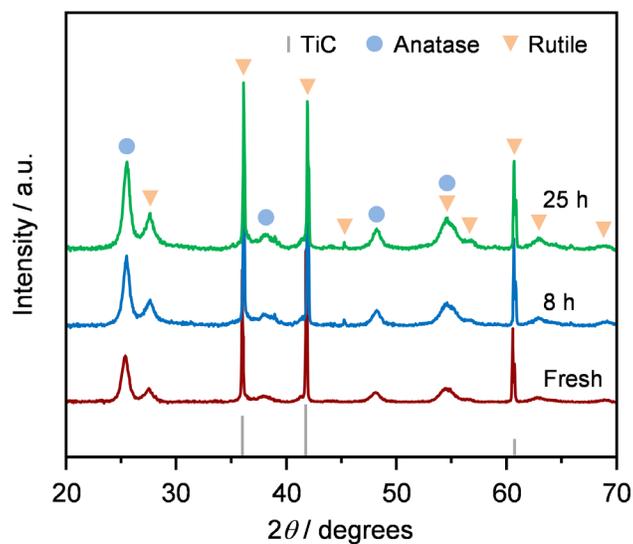
**Fig. S5** X-ray photoelectron spectroscopy depth profiles of TiC after treatment at 673 K in air, showing the relative oxygen and carbon composition as a function of the sputtering time, which is indicative of the content of titanium carbide and oxide in the TiC-673 sample.



**Fig. S6** Transmission electron micrographs of TiC after treatment in air at **a)** 623 K, **b)** 648 K, **c)** 723 K, **d)** and **e)** 1123 K, and **f)** 1273 K.



**Fig. S7** Rate of bromine production as a function of temperature in the catalytic oxidation of HBr over the catalysts. Temperature was decreased from the highest to the lowest value (solid) and then increased back to the starting point (open). Conditions:  $\text{HBr}:\text{O}_2:\text{He} = 4.5:9:86.5$ ,  $F_T/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$ ,  $T = 523\text{-}598 \text{ K}$ , and  $P = 1 \text{ bar}$ .



**Fig. S8** X-ray diffraction of fresh TiC-673 and after HBr oxidation at different times on stream, *tos*. Conditions: HBr:O<sub>2</sub>:He = 4.5:9:86.5,  $F_T/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$ ,  $T = 523\text{-}598 \text{ K}$ ,  $P = 1 \text{ bar}$ , *tos* = 8 and 25 h.