Supporting Information

Mesoporous and Graphitic Carbide-Derived Carbons as Selective and Stable Catalysts for the Dehydrogenation Reaction

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1. Synthesis of TiC-CDC

The reactive metal extraction from titanium carbide (Goodfellow; >99.8%; d_{mean} = 85 µm) was carried out in a horizontal hot-wall reactor setup, consisting of an alumina tube (l = 1500 mm; d = 33 mm) that is placed in a furnace (GERO Hochtemperaturöfen GmbH & Co. KG; HTRH 100-600). Experiments were conducted at 500–1585 °C using diluted chlorine in helium as extraction agent. All gas flows were controlled by mass flow controllers (Bronkhorst High-Tech). The gas flows were always adapted for a superficial velocity of 0.03 m s^{-1} and a chlorine concentration of 0.5–1.0 mol m^{-3} at the desired reaction temperature. After the chlorination, the resulting CDC was post-treated with diluted hydrogen in helium (1 mol m^{-3}) at reaction temperature and subsequently cooled down to room temperature under helium purge. For the reactive extractions at 500, 1500 and 1585 °C the annealing in hydrogen was carried out at 600, 1400 and 1400 °C, respectively. Full conversion of titanium carbide to carbon was proven by the mass loss during the chlorination as well as by XRD.

2. Nitrogen sorption

Additional to the data given in the manuscript, Figure S1 shows the high-resolution nitrogen sorption isotherms of TiC-CDC-800, -1300 and -1585.

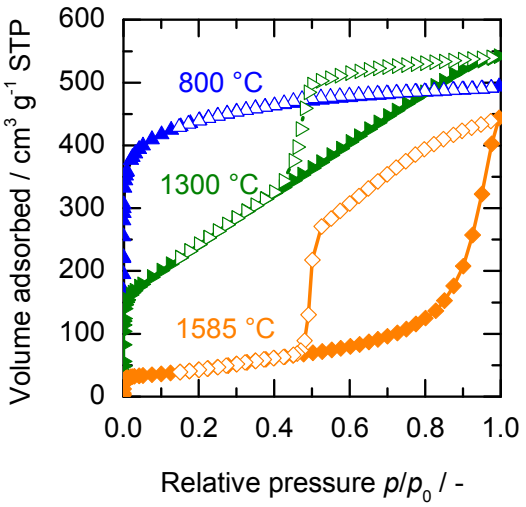

Figure S1. Nitrogen adsorption (closed symbols) – desorption (open symbols) isotherms of TiC-CDC synthesized at 800, 1300 and 1585 °C.

3. Raman analysis

The Raman spectra display two peaks centered at ca. 1330 and 1580 cm^{-1}, corresponding to the disorder-induced D and the graphitic G band (Figure S2A).[S1,2] At extraction temperatures above 1200 °C both the D and the G band become narrower and well separated. Additionally, a Raman feature around 2630 cm^{-1} starts to get observable, which is referred to the second order of the D band (G').[S3] A further increase of the synthesis temperature blue shifts the G' band to 2655 cm^{-1} at 1585 °C accompanied by the development of a shoulder at approx. 1610 cm^{-1} denoted as D'. The appearance of this band has been assigned to in-plane vibrations of outer parts of graphitic domains.[S4]

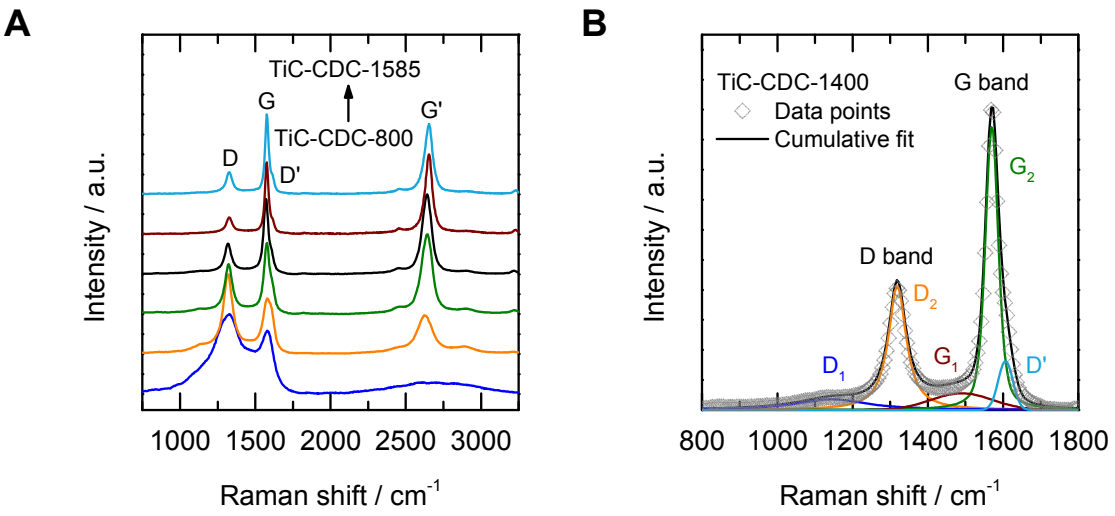

Figure S2. Raman analysis using a laser wavelength of 633 nm: A) Raman spectra of TiC-CDC synthesized at different temperatures and B) exemplary peak deconvolution for TiC-CDC-1400.

Raman data peak deconvolution of the D and G band was carried out by fitting four Lorentzian/Gaussian type peaks, to account for the shoulders at 1170 and 1510 cm^{-1} that activated carbons typically feature. Three spectra have been measured for each CDC material. An additional Lorentzian/Gaussian type peak is used for materials synthesized at 1300 °C or above in order to account for the shoulder at approx. 1610 cm^{-1}. The intensity ratio of the D_2 to the G_2 band was used to estimate the in-plane correlation length (L_a) as proposed by Tuinstra and Koenig [S5] and modified by several authors, especially for amorphous carbons by Ferrari et al..[S6] The results are summarized in Table S1.

Table S1. Raman characteristics of TiC-CDC synthesized from 800 to 1585 °C.

$T_{Syn.}$ / °C	D_2 band	G_2 band	D' band		
	Position / cm^{-1}	Position / cm^{-1}	Position / cm^{-1}	$I_{D2}\ I_{G2}^{-1}$ / -	L_a / nm
800	1324	1585	-	1.29	-[a)]
1200	1319	1588	-	1.57	5.3
1300	1323	1577	1613	0.77	10.8
1400	1325	1575	1613	0.41	20.3
1500	1325	1577	1613	0.42	19.6
1585	1325	1576	1612	0.31	26.8

[a)]: T-K relationship is not valid for unit sizes below 2 nm

In accordance with the XRD results, the in-plane crystallite size estimated from the intensity ratio of the D_2 and G_2 band increases with higher synthesis temperature. For instance, the length of the graphitic crystallites quintuples going from TiC-CDC-1200 to -1585.

4. TEM and EELS analysis

Samples were prepared by dispersing a small amount of the TiC-CDC powder in pure ethanol and subsequent ultrasonic treatment for five minutes. A drop of this dispersion was then placed on a copper grid with a holey amorphous carbon film.

In order to avoid anisotropy effects of the sample, all EELS measurements were obtained at magic angle condition. This experimental condition was achieved by a highly oriented pyrolytic graphite crystal (HOPG) where no significant changes were found in spectra when tilting the sample out of the c-axis. Carbon K-edge spectra of TiC-CDC synthesized at different temperatures along with the HOPG one are shown in Figure S3A. The measured spectra were deconvoluted by a Fourier-ratio method to remove multiple scattering after background subtraction. The peak at 285 eV stems from $1s \rightarrow \pi^*$ transition, which is characteristic for sp^2-hybridized carbon. The relative fraction of sp^2-hybridized carbon can thus be determined by equation (S1):

$$sp^2 = \frac{\left[\frac{area[\pi^*]}{area[\pi^* + \sigma^*]}\right]_{sample}}{\left[\frac{area[\pi^*]}{area[\pi^* + \sigma^*]}\right]_{100\%\, sp^2\ reference\ HOPG}} \qquad \text{(S1)}$$

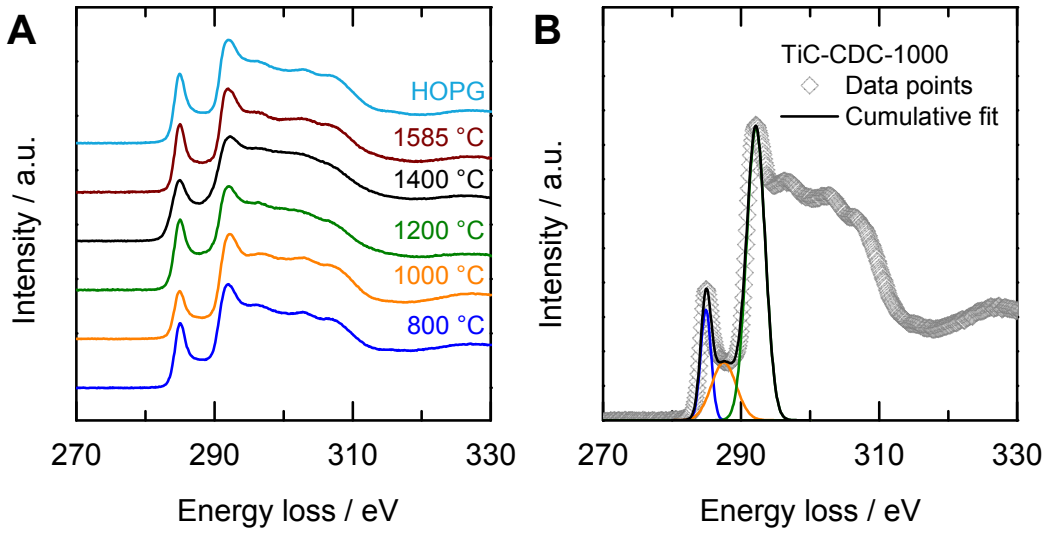

Figure S3. EELS characterization: A) Carbon K-edge spectra of TiC-CDC synthesized at different temperatures and HOPG reference spectrum; B) Exemplary spectra deconvolution for TiC-CDC-1000.

Equation (S1) yields 100% for purely sp^2-hybridized carbon of HOPG crystal. The respective areas in the formula are obtained by integrating three fitted Gaussian type peaks

centered at 285, 287.8 and 292.2 eV, respectively (Figure S3B). The first two of the three peaks are considered to describe transitions to the π^* state. The third one at 292.2 eV denotes the transitions to the σ^* state. Six spectra have been measured for each CDC materials to ensure that the set of spectra correctly reflects the sample. The determined average sp^2 fractions of TiC-CDC synthesized at temperatures ranging from 500 to 1585 °C are shown in Figure 2B.

5. Oxygen Surface Functionalization of TiC-CDC

Thermogravimetric analysis in inert gas was used to study the surface functionalization by temperature-programmed desorption (TPD). Figure S4 shows the DTG curves of as produced TiC-CDC-800 and -1200 as well as after sulfuric acid treatment and air oxidation. Both treatments introduced low-temperature desorbing groups e.g. carboxylic or sulfonic ones, which decompose till 400 °C. The associated weight loss represented by the integral of the DTG curve lowers going from a synthesis temperature of 800 to 1200 °C. The increasing graphitic crystallinity leads to a lower reactivity of the CDC material. Accordingly, under the same experimental conditions a minor content of functional surface groups results, which is in accordance with the literature.[S7]

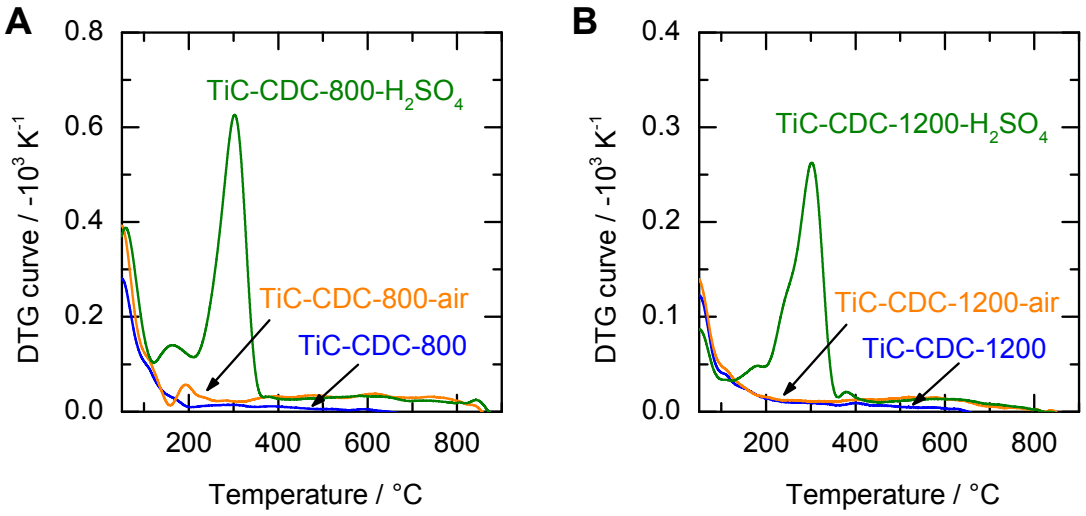

Figure S4. A) DTG curves for as produced TiC-CDC-800 and after oxidative treatment with sulfuric acid and in air; B) DTG curves for as produced TiC-CDC-1200 and after oxidative treatment with sulfuric acid and in air.

In order to support the TPD results, the elemental composition (C, H, N, S, O) was determined for the nitric acid treated TiC-CDC materials synthesized from 800 to 1500 °C. The data are given in Table S2. The non-carbon content is reduced from 30.5 over 10.6 to 2.0 wt.-% for the samples based on TiC-CDC-800, -1300 and -1500, respectively. Hence, the degree of functionalization consecutively lowers with increasing synthesis temperature. The elemental analysis further reveals that for CDC produced below 1400 °C nitrogen-containing groups are introduced.

Table S2. Elemental analysis for TiC-CDC materials treated with nitric acid for 2 h at 90 °C.

	TiC-CDC-XXX-HNO_3				
wt.-%	800	1200	1300	1400	1500
C	69.5	84.1	89.4	95.4	98.0
O	28.6	15.1	10.3	4.6	2.0
N	0.5	0.4	0.1	-	-
H	1.4	0.4	0.2	-	-
S	-	-	-	-	-

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