<u>Supplementary Information</u>

Strategies to Design Efficient Silica-Supported Photocatalysts

for Reduction of CO_2

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Experimental section

Catalyst preparation

The following chemicals were obtained and used in the synthesis of the catalysts without further treatment: Tetraethyl orthosilicate (TEOS, +98% ACROS), triethanolamine (TEA, 97% ACROS), tetraethylammonium hydroxide (TEAOH, 35% Aldrich), titanium (IV) butoxide (97%, Sigma Aldrich), zinc acetate dihydrate (>98%, Sigma Aldrich) and chromium (III) nitrate nonahydrate (99%, Sigma Aldrich).

Different samples of functionalized TUD-1 were prepared: 1) A series of Ti-TUD-1 (Si/Ti = 1000-10) [R1, R2] labelled as Ti-x, where x represents the wt-% of Ti. 2) A sample of ZnO-Ti-TUD-1, where the ratio Si/Ti = 100 and the ratio Si/Zn = 10. This sample is labelled Ti1-Zn10. 3) A sample of ZnO-TUD-1 with Si/Zn = 10, labelled as Zn-10. 4) A sample of Cr-Ti-TUD-1 with Si/Ti = 100 and Si/Cr = 100, the sample labelled as Ti1-Cr1. 5). A sample of Cr-TUD-1 with Si/Cr ratio = 100, labelled as Cr-1 [R3].

All samples were prepared through the well-established one-pot hydrothermal synthesis procedure described earlier [R4]. The synthesis procedure consists of aging, drying, hydrothermal treating, and finally calcination of a homogeneous mixture of TEOS, TEA, TEAOH, H_2O and the metal precursors with a molar ratio of 1 SiO_2: 1 TEA: 0.5 TEAOH: 11 H_2O: xMO.

Catalysts characterization

The X-ray diffraction patterns (XRD) were recorded on a Bruker D2 model X-ray diffractometer using Cu K_α radiation (λ=1.54 Å) as the X-ray source operating at 30 kV and 10 mA over the 2θ range 10-90°.

The diffused reflectance UV-visible spectra (DRS) of the samples were recorded by an UV-vis spectrometer (EVOLUTION 600, Thermal Scientific) with a diffuse reflectance accessory using $BaSO_4$ as reference at room temperature.

Nitrogen adsorption/desorption isotherms were recorded on a Micromeritics Tristar System ASAP 2400at 77 K. Samples were previously evacuated at 573 K and 10^{-3} Pa for 24 h. The pore size distribution was calculated from the adsorption branch using the Barret-Joyner-

Halenda (BJH) model. The BET method was used to calculate the surface area (S_{BET}) of the samples, while the mesopore volume (V_{meso}) and pore diameter (D_{meso}) were determined using the t-plot method.

X-ray absorption fine structure (XAFS) measurements (Zn K-edge, 9659 eV) were carried out at HASYLAB (DESY, Hamburg, Germany) at beamline C using a double-crystal Si(111) monochromator, which was detuned to 65% of maximum intensity to exclude higher harmonics in the X-ray beam. The spectra were recorded in transmission mode at liquid nitrogen temperature to suppress thermal disorder. For the measurements, samples were pressed in self-supporting pellets (13 mm diameter) and wrapped with Kapton tape. All spectra were measured simultaneously with the reference spectrum of a zinc foil placed between second and third ionisation chambers. This allowed absolute energy calibration. The spectra of Zn foil and ZnO, which were used as reference, were collected under the same conditions. All spectra were measured 2 times to ensure their reproducibility.

Analysis of the EXAFS spectra was performed with the software VIPER for Windows. In the spectra of the absorption coefficient μ, a Victorian polynomial was fitted to the pre-edge region for background subtraction. A smooth atomic background μ_0 was evaluated using a smoothing cubic spline. The Fourier analysis of the k^2-weighted experimental function $\chi = (\mu - \mu_0)/\mu_0$ was performed with a Kaiser window. The required scattering amplitudes and phase shifts were calculated by the *ab initio* FEFF8.10 code for the Wurtzite ZnO structure. The fitting was done in the k- and r-spaces. The shell radius r, coordination number N, Debye-Waller factor σ^2 and adjustable "muffin-tin zero" ΔE were determined as fitting parameters. The errors of the fitting parameters were found by decomposition of the statistical χ^2 function near its minimum, taking into account maximum pair correlations.

TPD measurements were performed in a stainless-steel flow setup equipped with a calibrated online mass spectrometer (Balzers GAM400). In a typical experimental sequence 50 mg of catalyst were placed in a quartz-lined stainless steel U-tube reactor. A thermocouple was placed into the catalyst bed to measure the temperature during the desorption experiments. The sample was pre-treated at 400 °C with a heating ramp of 10 K min^{-1} in 50 NmL min^{-1} 1% O_2/He and then kept at 400 °C for 1 h. After cooling to room temperature the reactor was purged with He, and subsequently CO_2 adsorption was

performed with a flow rate of 50 mL min^{-1} 4.1% CO_2/He for 15 min. After purging with He for 30 min the temperature was increased to 400 °C with a heating ramp of 10 K min^{-1} and held at this temperature for 1 h. During desorption the concentration of CO_2 in He was measured continuously.

High-Resolution Transmission Electron Microscopy (HR-TEM) was carried out on a Philips CM30UT electron microscope with a field emission gun as the source of electrons operated at 300 kV. Samples were mounted on a copper-supported carbon polymer grid by placing a few droplets of a suspension of the ground sample in ethanol on the grid, followed by drying at ambient conditions.

In-situ Diffuse and Reflectance Infrared Fourier Transform spectroscopy was carried out using a Bruker Vertex 70 spectrometer equipped with a Liquid N_2 cooled MCT detector, and a three window DRIFTS (Diffuse and Reflectance Infrared Fourier Transform Spectroscopy) cell. Two ZnSe windows allowed IR transmission, and a third (Quartz) window allowed the introduction of UV/Vis light into the cell. Prior to the illumination experiments, 25 mg of the as-synthesized Ti-TUD-1 and Cr-Ti-TUD-1 catalysts were heated up to 393 K in He (30 mL/min) for 0.5 h, in order to remove the majority of adsorbed water. A spectrum was recorded of this state of the catalysts, to serve as background for a spectral series of formaldehyde adsorption. Formaldehyde was introduced in the cell by evaporation of a 10 weight percent formaldehyde water mixture into a flow of 20 mL/min of He. After exposure of the catalyst to this flow for 30 minutes, the lines to the cell were closed, and illumination started. The last spectrum recorded after introduction of formaldehyde served as background for the series recorded during illumination. In-situ IR signals were recorded every 10 min under UV/Vis light irradiation (100 Watt Hg lamp (Dr. Groebel), wavelength range 250 – 600nm)).

Photocatalytic performance

Catalyst pre-treatment

In order to remove any possible residual carbon [R5], the socalled moisture/He test was carried out, in which the catalysts were illuminated in a He/water vapour environment. Gas samples were withdrawn and analysed by GC. This process was continued until zero

hydrocarbons were recorded, which is an indication that the sample is clean and ready for the photocatalytic test.

Photocatalytic performance evaluation

The photocatalytic reduction of CO_2 in the presence of H_2O vapour was evaluated in a home-made multi-cell photocatalytic set-up. The set-up consists of 12 identical cylindrical reactors (inner volume 50 mL), which are connected to a sample loop for gas dosage and sampling. The applied light source is a 120W high-pressure mercury lamp with a spectrum ranging from 280 to 650 nm. The reaction was conducted with a ratio 0.5 of CO_2 (38 µmol) over H_2O (76 µmol). All reactors were operated in batch mode and illuminated for 8 h. The production of hydrocarbons was monitored by a compact gas chromatograph equipped with Molsieve 5A and capillary Porabond Q columns connected to a TCD detector (used for separation of H_2, O_2, N_2, CO and CH_4). A second Porabond Q column connected to an FID detector was used for separation and detection of C_1-C_4 alkanes and alkenes. Concentrations were analyzed with an accuracy of ±0.5 ppm. In evaluating the reaction, 100 mg of the catalysts were distributed evenly at the bottom of the reactor to create a uniform layer with a thickness of approximately 1-2 mm. The reactors were evacuated down to 3 mbar and then the CO_2/He mixture saturated with water vapor was introduced. The evacuation/filling cycle was repeated three times, followed by initiation of illumination.

The reusability of the Ti-1 sample

The stability and reusability of the Ti-1 sample was evaluated as follows. The gases produced in the first experiment were removed by evacuation from the reactor, and then a fresh CO_2/H_2O mixture introduced. This process was repeated six times without any treatment of the catalyst.

Hydrocarbon degradation

The study of hydrocarbon degradation (the backward reactions) was carried out by using a standard gas mixture of 1 volume% of CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 in Helium. By dilution, a He stream containing 25 ppm of each component and 4 mol% of water vapour was introduced into the reactors containing the catalyst powders. Evacuation/filling cycles were

repeated at least three times before lamp ignition and start of the degradation experiments.

The photocatalytic degradation of the gas mixture was monitored by gas chromatography.

Table S1. The elemental analysis, textural properties and colour of the as prepared samples.

| Sample	Code	Elemental analysis		Texture properties			Colour
		Si/Ti	Si/M[a]	S^b (m^2/g)	V^c (cm^3/g)	D^d (nm)	
Ti-TUD-1	Ti-1	112	0	628	1.07	9.1	White
ZnO-Ti-TUD-1	Ti1-Zn10	109	9.8	735	0.82	5.1	White
Zn-TUD-1	Zn-10	0	9.98	680	0.91	6.3	White
Cr-Ti-TUD-1	Ti1-Cr1	108	111	625	1.28	10.2	Yellow
Cr-TUD-1	Cr-1	0	118	590	1.43	8.8	Yellow

[a] M = Zn or Cr
[b] BET Specific surface area
[c] Mesopore volume
[d] Mesopore diameter
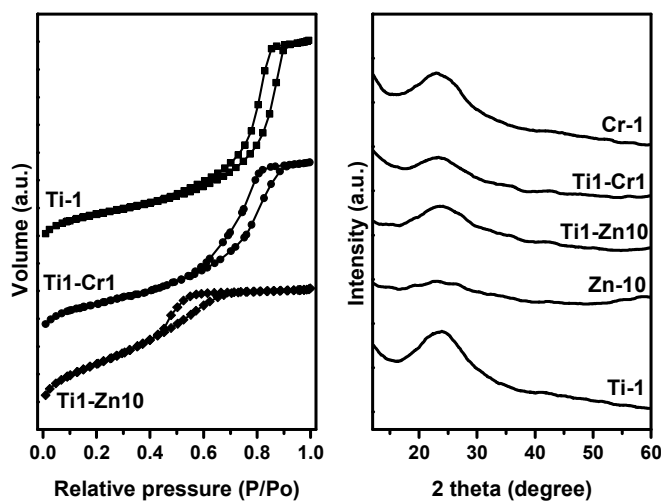
Figure S1. Left panel: The N_2 isotherms of the Ti-1 sample compared to the modified samples, Ti1-Cr1 and Ti1-Zn10. Right panel: Wide angle XRD patterns of the prepared samples.

Figure S2
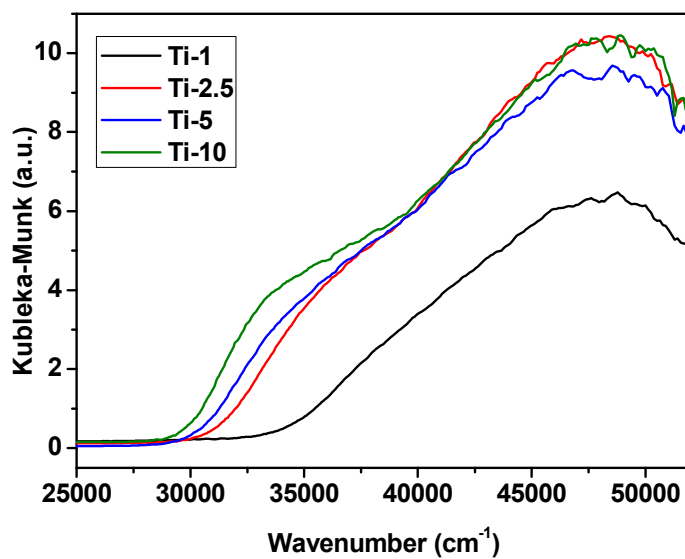
Figure S2. UV-DRS spectra of Ti-TUD-1 samples. Spectra were measured under dried conditions where samples were heated over-night at 180°C.
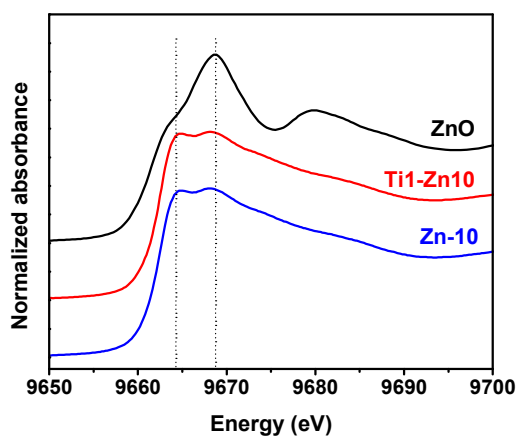
Table S2. The % of tetrahedral Ti^{4+} in Ti-TUD-1 samples.

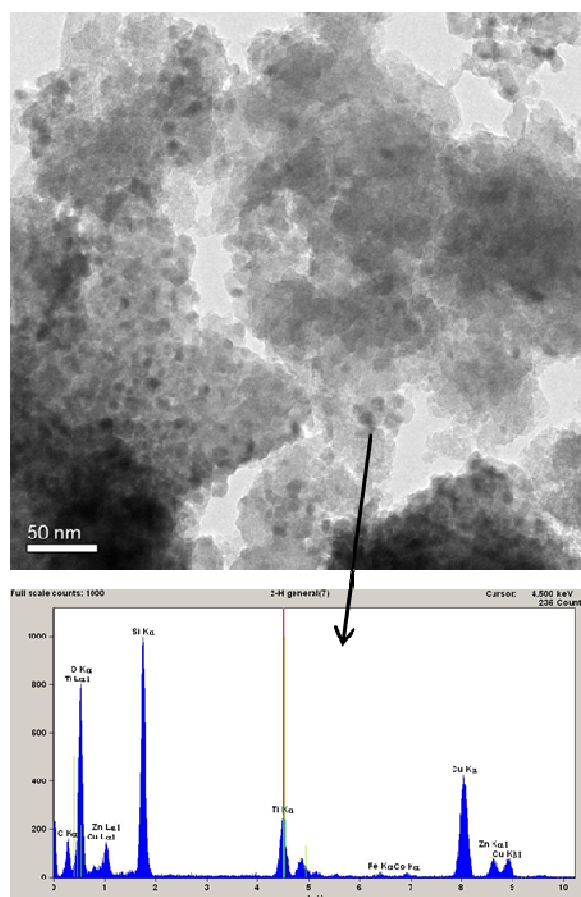| Sample	Ti^{4+} tetrahedral*
Ti-1	99.9%
Ti-2.5	68%
Ti-5	65%
Ti-10	58%

* The tetrahedral Ti^{4+} % was calculated by dividing the area of the signal maximizing at 48000 cm^{-1} by the sum of the areas of the 48000 cm^{-1} and 35000 cm^{-1} signals.

Figure S3
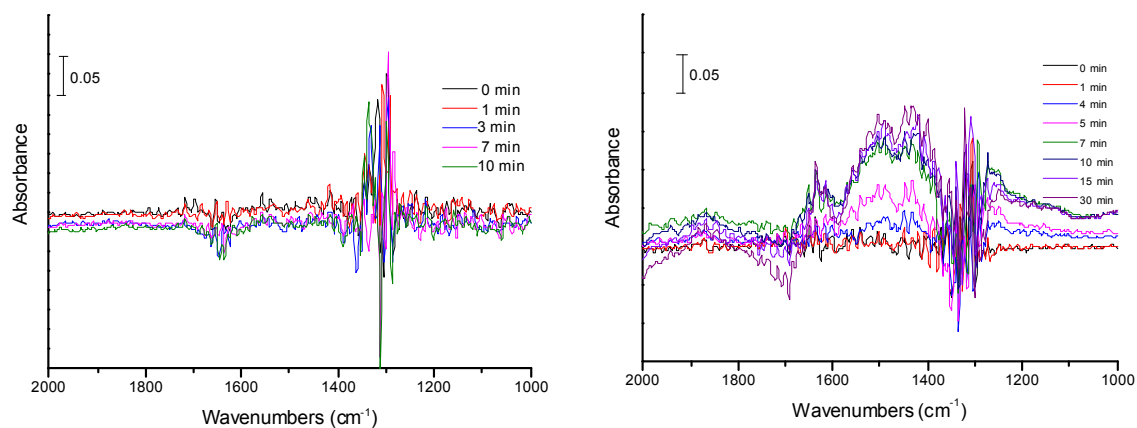

Figure S3. ZnK XANES spectra of Zn-10 and Ti1-Zn10, as compared to reference ZnO.

Figure S4. Top panel: HR-TEM micrograph of the Ti1-Zn10 sample. Bottom panel: A print-screen image of the EDX analysis of the sample. The arrow signals the area focused on for the analysis.
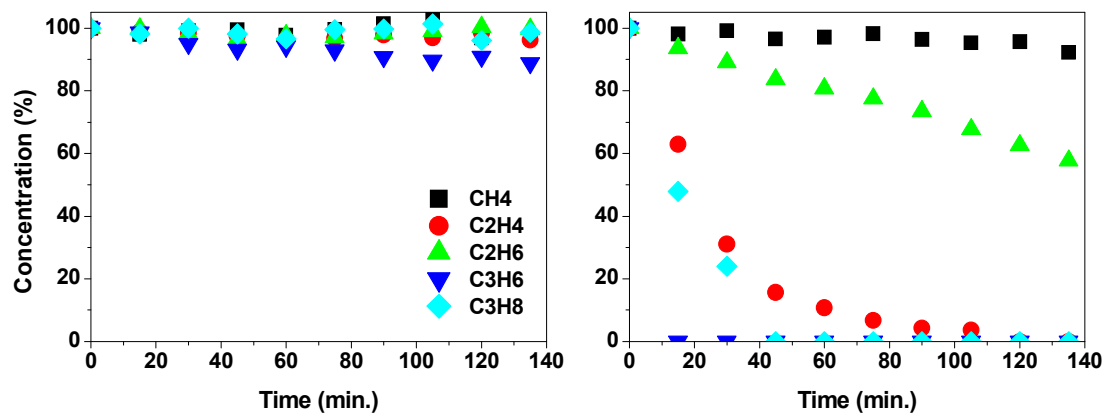
Figure S5

Figure S5. Infrared spectral development of Ti1-Cr1 (left) and Ti1-Zn10 (right) by dosing pure CO_2 (1 atmosphere) to the catalyst samples. CO_2 sorption is not apparent for the Ti1-Cr1 catalyst, whereas absorption bands at wavenumbers expected for (bi)carbonate species are clearly developing in the case of the Ti1-Zn10 catalyst.
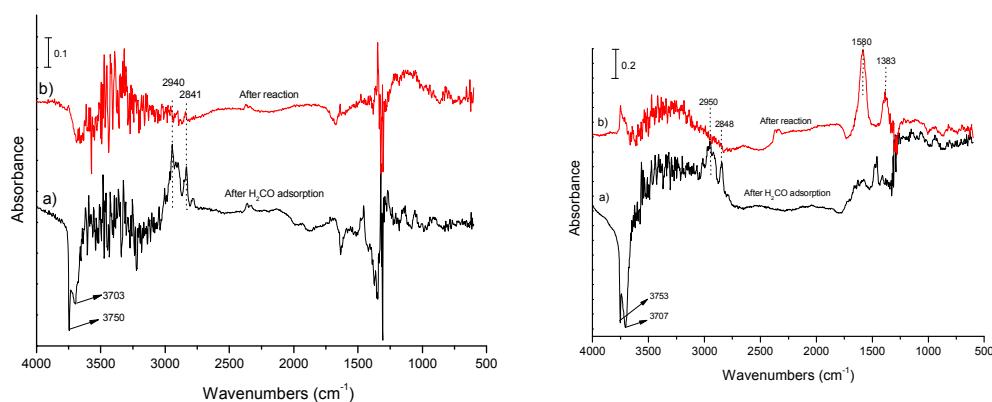
Figure S6
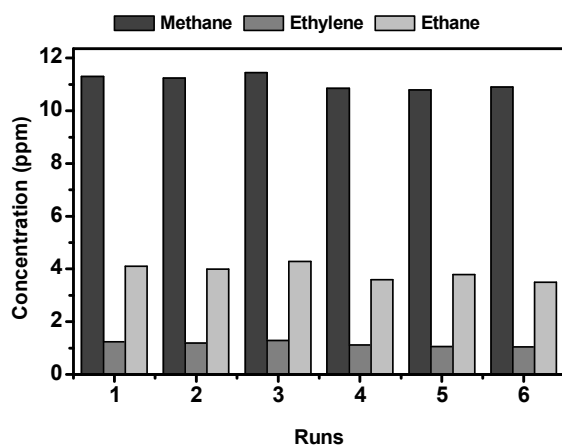
Figure S6. The concentration of the different hydrocarbons produced after 8 hours of illumination, for a repetition of 6 runs over the same Ti-1 sample, without any treatment in between runs.

Figure S7

Figure S7. The degradation profiles of the different hydrocarbons over Ti-10 (Left panel) and Hombikat TiO_2 (Right panel).

**Figure S8**

Figure S8. DRIFT spectra recorded after adsorption of formaldehyde/water (spectrum a), recorded against a background of the catalyst dried at 393 K), followed by illumination (spectrum b), recorded after 1 hour, against spectrum a) as background). The left panel contains the spectra of Ti-1, and the right panel of Ti1-Cr1. Comparing the two catalytically active materials, it is evident that formaldehyde is effectively oxidized to formate (1580 and 1383 cm^{-1}) over the Cr containing catalytic formulation, whereas formate formation is not observed for the catalyst without Cr. This supports the hypothesis that besides a high activity for oxidation of hydrocarbon products, intermediates (formaldehyde) are likely to show very different chemistry over supported Cr-containing catalysts as compared to Ti-only.

Table S3. The first order rate constant of the hydrocarbons degraded over the different Ti-TUD-1 samples. The obtained negative values are due to slight production of methane and/or ethane due conversion of carbon contamination in the ZnO containing samples.

Hydrocarbon	The first order rate constant $k \times 10^{-3}$ (min^{-1})				
	Ti-1	Ti1-Zn10	Zn-10	Ti1-Cr1	Cr-1
Methane	0.08	0.02	-2.49	1.02	0.97
Ethylene	0.10	4.5	11.6	80.3	2.06
Ethane	-0.33	-0.13	-1.76	5.9	0.05
Propylene	0.35	17.0	44.7	640.0	18.9
Propane	0.85	1.66	7.01	125.8	2.13

References

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[R4] M.S. Hamdy, Ph.D. Dissertation, TU Delft, The Netherlands, **2005**.

[R5] C.-C. Yang, Y.-H. Yu, B. van der Linden, J.C.S. Wu, G. Mul, *J. Am. Chem. Soc*. **2010**, *132*, 8398-8406.

[R6] C.-C. Yang, J. Vernimmen, V. Meynen, P. Cool, G. Mul, *J. Catal*. **2011**, *284*, 1-8.