**Experimental section**

**Catalyst preparation**

Plain SBA-15 was synthesized as described by Zhao et al. [1] in a variant, where the batch was stirred at 35 °C for 12 h after addition of Si(OEt)$_4$, and calcination was carried out at 650 °C in air.

Ti-SBA-15 was synthesized according to Melero et al. [2]. 4.00 g Pluronic P123 were dissolved in 125 mL 2M HCl at 40 °C. 0.51 g Cp$_2$TiCl$_2$ (Strem) were added and the resulting mixture was stirred at 40 °C for 3 h. 9 mL Si(OEt)$_4$ were added and stirred for 20 h at 40 °C. The obtained slurry was then kept at 100 °C for 24 h, filtered, washed and dried overnight to give a white powder. The organic structure directing agent was removed via calcination in air. For this purpose the sample was heated at 1 K/min to 650 °C, kept at 650 °C for 16 h and then cooled to RT with 1 K/min. 2.27 g Ti-SBA-15 were obtained.

Vanadia catalysts were obtained by incipient wetness impregnation of the supports mentioned above, i.e. SBA-15 and Ti-SBA-15 (nominal vanadium content was fixed to 2.8 wt%). In general, 0.6 g of support were heated to 70 °C whilst 39 mg NH$_4$VO$_3$ (Sigma-Aldrich) were dissolved in 4 mL H$_2$O at 60 °C. The support was then impregnated by addition of portions of 200 μL of aqueous NH$_4$VO$_3$. Prior to calcination the sample was kept at 70 °C for 12 h and then heated up to 650 °C in air at 1 K/min and kept there for 16 h. After cooling to RT at 1 K/min the VO$_x$-containing samples were obtained; they were denoted as V/SBA-15 and V/Ti-SBA-15.

**Catalyst characterization**

Bulk vanadium content was determined using a Varian 715-ES ICP optical emission spectrometer (ICP-OES). The specimen were dissolved by hydrofluoric acid/aqua regia and analyzed after a microwave treatment at 473 °C and 80 bar.
Specific surface area and pore size distribution were determined from N$_2$-physisorption data obtained using a NOVA 4200e instrument (Quantachrome). As a pre-treatment, samples were outgassed and dried for 2 h at 200 °C at reduced pressure. Data analysis of isotherm data was carried out according to methods described by Brunauer, Emmett, Teller (BET) [3] and Barrett, Joyner, Halenda (BJH) [4].

UV-vis spectra were recorded via fibre optic spectrometers (AvaSpec 2048, Avantes) or using Varian Cary 400 equipped with a Harrick Praying Mantis High Temperature Reaction Chamber. Spectra were recorded in diffuse reflectance (DR). Dehydration was carried out by heating the sample to 240 °C in He for 20 min.

Raman spectra at an excitation wavelength of 442 nm (12 mW, 50 sec exposure time) were recorded using a Raman Microscope (inVia by Renishaw). Samples were measured in hydrated state.

Temperature-programmed reduction (H$_2$-TPR) of the vanadia-containing catalysts was carried out using an Autochem 2920 by Micromeritics after pre-oxidation using 5% O$_2$ in Ar (20 mln/min, pre-dried gas) and heating the sample to 650 °C at 10 K/min keeping it at 650 °C for 30 min. For subsequent reduction in 5% H$_2$ in Ar (20 mln/min, pre-dried) the same temperature program was used.

A JEM-ARM200F (JEOL) was employed at 200 kV for transmission electron microscopy (TEM) measurements using aberration correction by a CESCOR (CEOS) for STEM. In addition with TEM imaging, an elemental analysis was carried out using energy dispersive X-ray spectroscopy (EDX).

**Catalytic tests**

A home-made quartz reactor with an inner diameter of 10 mm was used for the catalytic tests. Feed gases (CH$_4$, O$_2$) were supplied from commercial suppliers (5.0, Air Liquide, Germany; Linde Gas, Germany) and used without further purification. Flow rates were varied and adjusted using thermal mass flow controllers (EL-flow, Bronkhorst-Mättig). A reactant molar ratio of CH$_4$: O$_2$ = 9: 1 was used and the space velocity (GHSV) was varied from 160,000 to 360,000 L/kg$_{cat}$h. Typically 50 mg catalyst was diluted with corundum 1: 10 w/w. All catalytic tests were carried out using granules of 600 to 800 micron size. These were obtained by pressing the catalyst powder, crushing the obtained tablets in a mortar followed by fractional sieving.

Product gas analysis was carried out without any condensation via online IR spectral analysis and linear combination of bands to fit the measured spectrum using a Calcmet v12.4 device (Gasmet CX4000, Ansyco).

For calculation of conversion and selectivity measured concentrations (vol%) were related to a reference (ref) taken for 10-40 min at below 450 °C (i.e. zero conversion).
Methane conversion was calculated using the equation given below, where $c_{CH_4,rxn}$ stands for the concentration of methane at the reactor outlet:

$$X_{CH_4} = \frac{c_{CH_4,ref} - c_{CH_4,rxn}}{c_{CH_4,ref}} \times 100\%$$

At methane conversion of <5%, the reaction was assumed to be constant in volume for all cases. Otherwise volumetric flow was checked using a soap bubble gas flowmeter at room temperature with a precision of +/- 5%. For constant flow, $S_{HCHO}$ was determined according to the following formula:

$$S_{HCHO} = \frac{c_{HCHO}}{c_{CH_4,ref} - c_{CH_4,rxn}} \times 100\%$$

As cross method, formaldehyde was collected in a cold trap and titrated. Precisely, an excess of 1.0 M Na$_2$SO$_3$ was added to the trapping solution. This led to formation of NaOH$_{aq}$ which was back-titrated using 0.2 M H$_2$SO$_4$ and indicating the equivalence point by thymolphthalein.
Data section

**BET sorption isotherms and BJH analyses**

**Figure S1**: Nitrogen sorption isotherms of a) undoped SBA-15, pure and VOₓ impregnated, and c) Ti-doped SBA-15, pure and VOₓ impregnated as well as b) and d) respective pore size distributions calculated according to the BJH method.
**TEM investigations**

**Figure S2:** TEM images of V/SBA-15 in (a) TEM mode and (b-d) STEM dark-field mode.
Figure S3: STEM images of V/Ti-SBA-15 in (a,b) bright-field mode and (c,d) dark-field mode.