Supplementary Material (ESI) for Green Chemistry
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Supporting information for the article

Marrying gas power and hydrogen energy: A catalytic system for combining methane conversion and hydrogen generation

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Fig. S1 and S2 show the carbon balance and hydrogen yield for all catalysts at 400-550 °C (Fig. S1: catalysts 1–10, Fig. S2: catalysts 11–21). The data show that hydrogen generation occurs simultaneously with a drop in carbon balance (i.e. coking).

Materials and instrumentation
Chemicals were purchased from Sigma-Aldrich or Merck and used as received. Gasses were purchased from Air Liquide and had a purity of 99.5% or higher. Powder X-Ray diffraction measurements were performed using a Philips PW-series X-Ray diffractometer with a Cu tube radiation source (λ = 1.54 Å), a vertical axis goniometer and a proportional detector. The 2θ detection measurement range was 10 °–93 ° with a 0.02 ° step size and a 5 second dwell time. GC analysis was performed on two Agilent instruments, one equipped with a Poraplot Q column to separate CO2 and CH4 (He carrier gas), and one equipped with a 5Å molsieve column to separate H2, CO, CH4 and O2 (Ar carrier gas). All catalytic tests were performed using the “SWITCH 16” setup (AMTEC GmbH), allowing for the testing of up to 16 catalysts simultaneously. Thermodynamic calculations were performed using the Outokumpu HSC Chemistry software package (Version 4.1).

Procedure for testing catalytic activity
The “SWITCH 16” system enables testing of a batch of sixteen catalysts at a time. The reaction mixture is fed to one of the reactors, and the exit flow of this reactor is directed to the GC's for analysis. Meanwhile, an oxygen/helium flow is fed to the remaining reactors to maintain the sample's integrity. The reactors are stainless steel tubes with an inner diameter of 4.7 mm each fitted with a thermocouple. In a typical experiment, 100 – 150 mg of sample (125–212 μm, bed volume 0.1–0.15 cm3) was placed between quartz wool plugs in the reactor, and the reactors were placed in the oven. The reaction mixture was led to an empty reference reactor, and the oven was heated to the first reaction temperature at 180 °C/h, with the other reactors under oxygen flow (20% O2/He). When the temperature was reached, the reaction mixture, consisting of 20% v/v CH4 and 30% v/v O2 in He, was fed to each reactor consecutively for 20 min, and two GC analysis were
performed after 7 and 14 min. When this was complete, the reaction mixture was directed to the reference reactor and the oven was heated to the next set point. This way, all reactors were analysed from 400 – 550 °C at 50 °C intervals. The total flow rates were kept at 50 mL/min in each step.

**Fig. S1** The carbon balance (bars) and hydrogen yield (●) for catalysts 1–10 at 400-550 °C. Reaction conditions: 100–150 mg catalyst, 2:3:5 CH₄/O₂/Ar at a total flow rate of 50 mL/min. The hydrogen yield is the hydrogen detected during the experiments, expressed as a percentage of the maximum amount of hydrogen that can be obtained from the methane feed. The maximum yield of 100% is therefore 2 moles H₂ per mole of CH₄.

**Fig. S2** The carbon balance (bars) and hydrogen yield (●) for catalysts 11–21 at 400-550 °C. Reaction conditions: 100–150 mg catalyst, 2:3:5 CH₄/O₂/Ar at a total flow rate of 50 mL/min. The hydrogen yield is the hydrogen detected during the experiments, expressed as a percentage of the maximum amount of hydrogen that can be obtained from the methane feed. The maximum yield of 100% is therefore 2 moles H₂ per mole of CH₄.