A family of oxide/carbide and oxide/nitride nanocomposites

Z. Schnepp, M. J. Hollamby, M. Tanaka, Y. Matsushita, Y. Xu and Y. Sakka

Supplementary Information

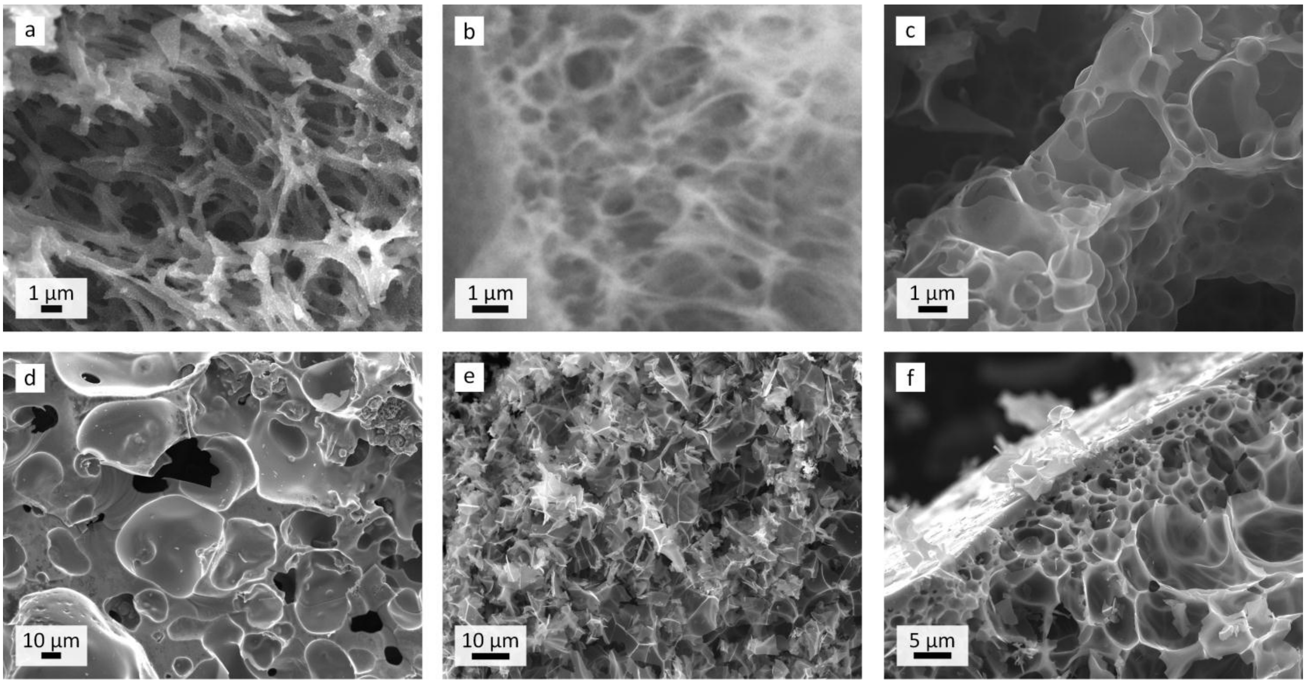

Figure S1 Scanning electron microscope images of a) TiO_2/Fe_3C, b) CeO_2/Fe_3C, c) MgO/Fe_3C, d) TiO_2/WN, e) CeO_2/WN and f) MgO/WN. NB: Sample c is analogous to our previously reported MgO/Fe_3C sample but the previously reported samples were prepared with much less polymer to optimize the carbon catalyst (in the previous report the MgO/Fe_3C samples were etched with acid to prepare porous carbons).

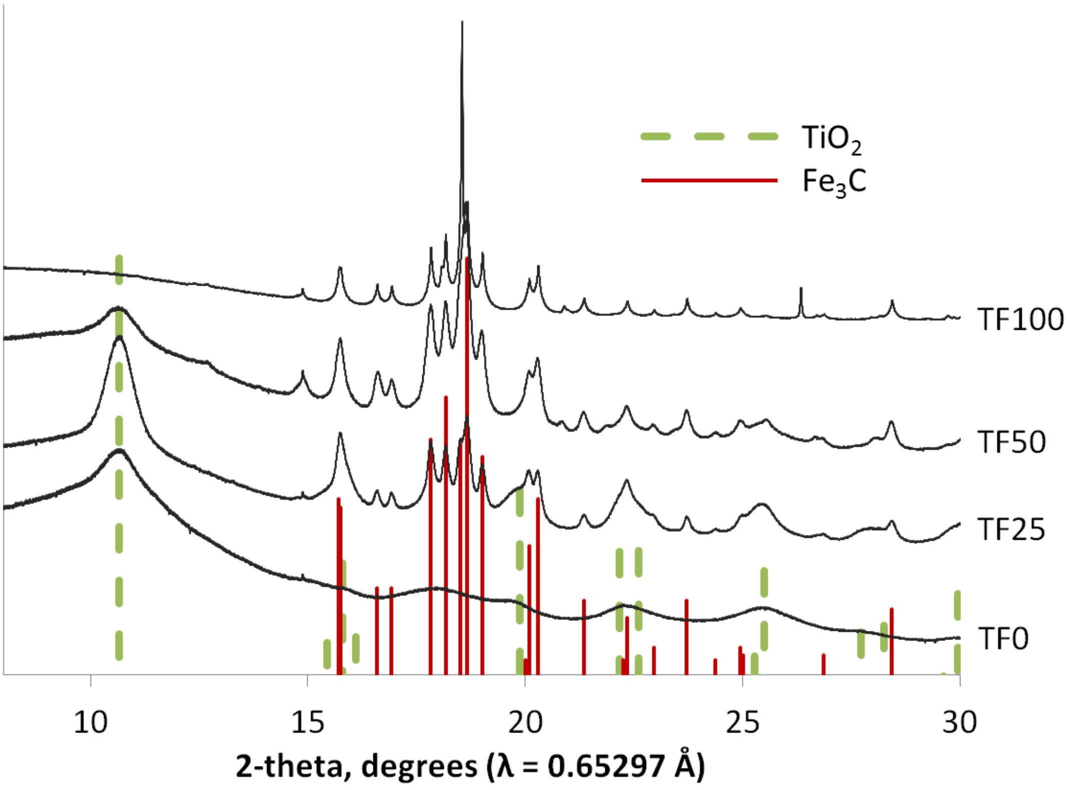

Figure S2 Powder X-ray diffraction patterns for TiO_2/Fe_3C samples prepared at various ratios from 0 mol% iron (TF0) to 100 mol% iron (TF100).

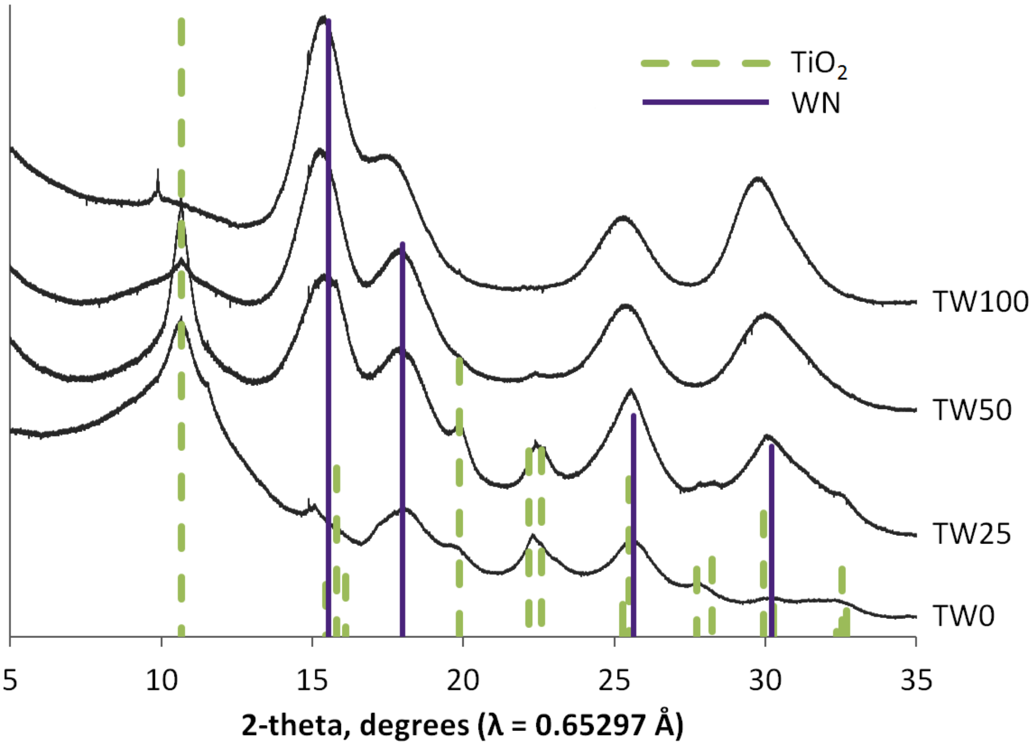

Figure S3 Powder X-ray diffraction patterns for TiO_2/WN samples prepared at various ratios from 0 mol% tungsten (TW0) to 100 mol% tungsten (TW100). The broad peak in sample TW0 at 2θ ≈ 17.5° indexes to TiO and the very minor sharp peaks fit the pattern for rutile.

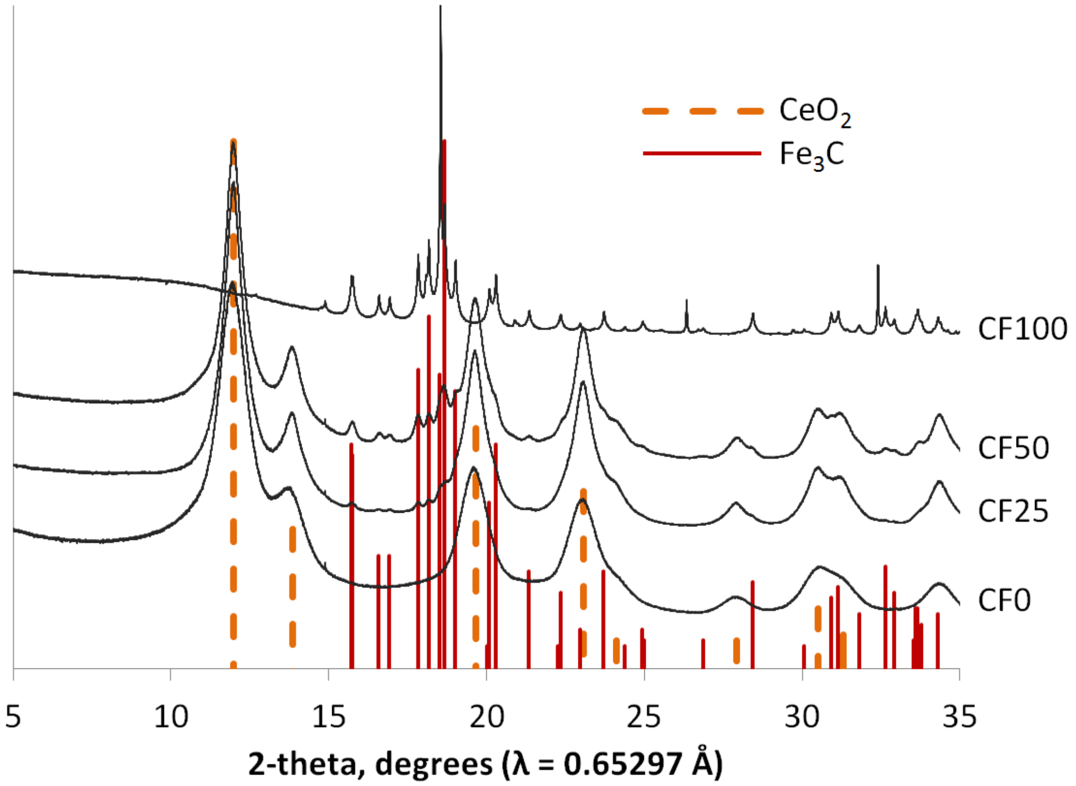

Figure S4 Powder X-ray diffraction patterns for CeO_2/Fe_3C samples prepared at various ratios from 0 mol% iron (CF0) to 100 mol% iron (CF100).

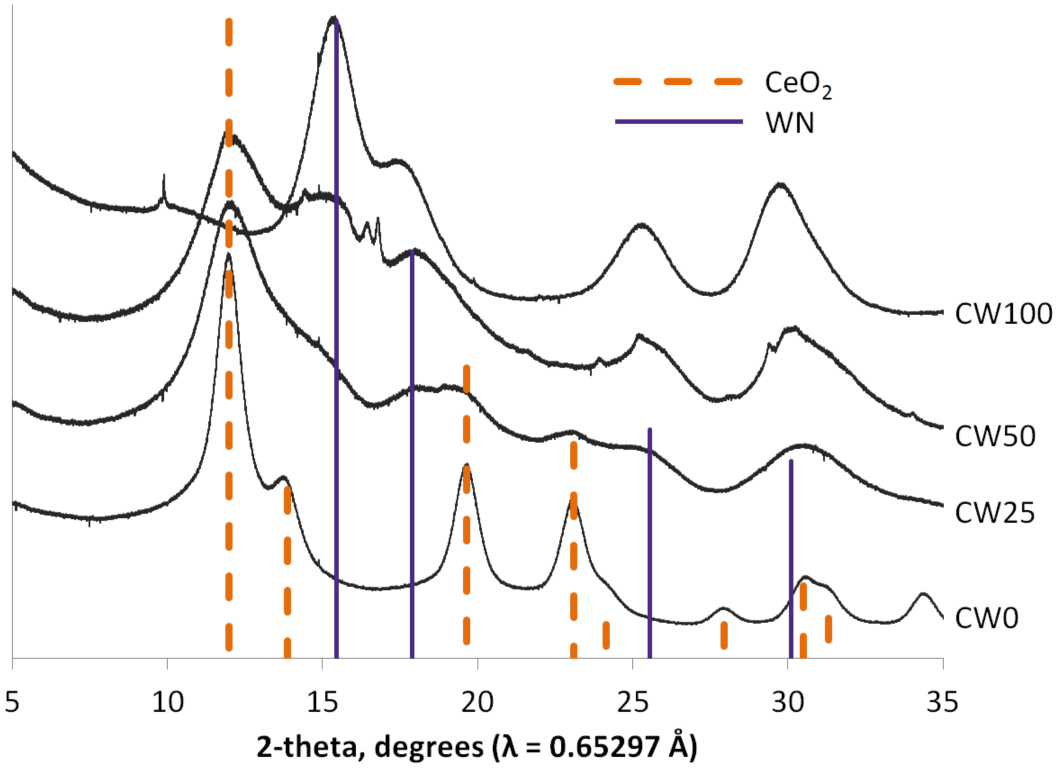

Figure S5 Powder X-ray diffraction patterns for CeO_2/WN samples prepared at various ratios from 0 mol% tungsten (CW0) to 100 mol% tungsten (CW100). Additional small sharp peaks in CW50 correspond to small amounts of WC and W

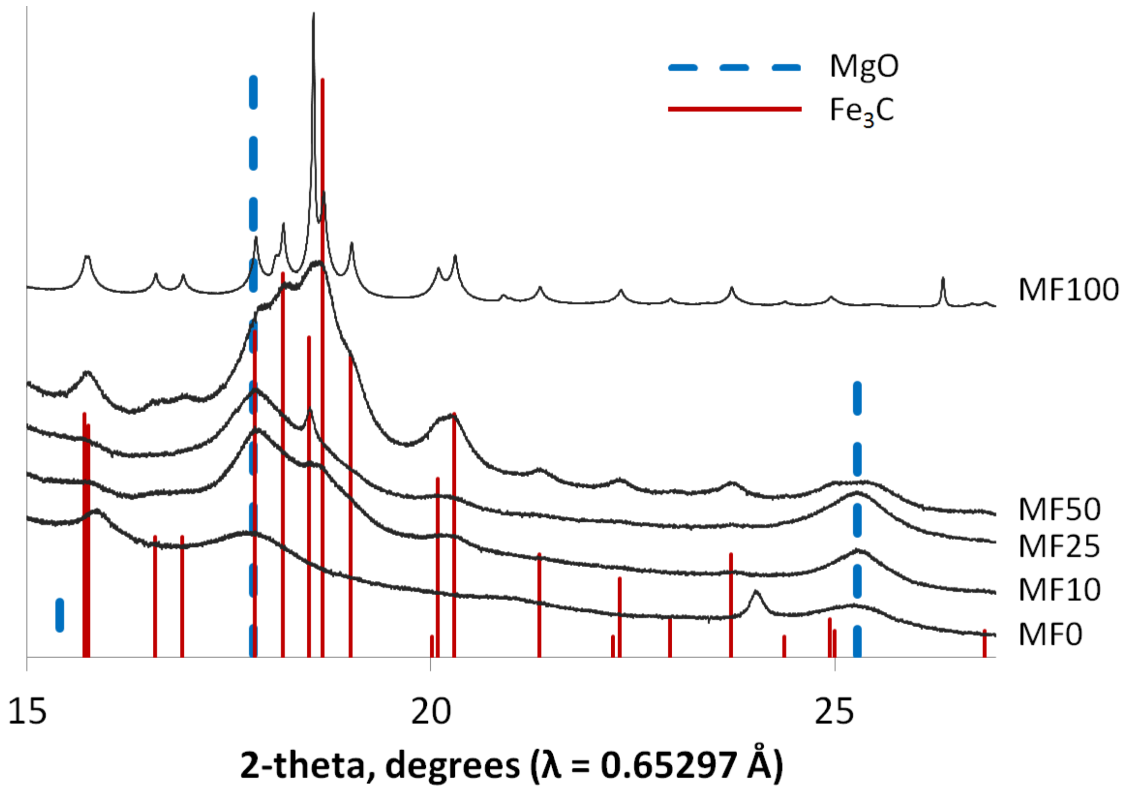

Figure S6 Powder X-ray diffraction patterns for MgO/Fe_3C samples prepared at various ratios from 0 mol% iron (MF0) to 100 mol% iron (MF100). The small, sharp peak in MF25 corresponds to Fe.

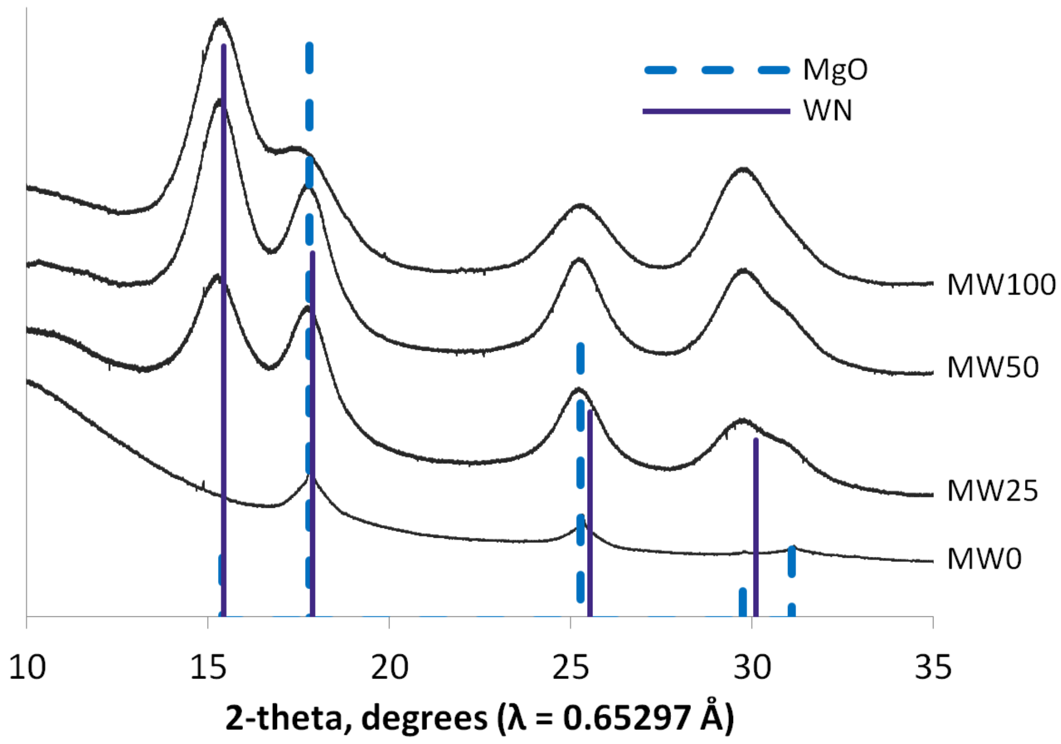

Figure S7 Powder X-ray diffraction patterns for MgO/WN samples prepared at various ratios from 0 mol% tungsten (MW0) to 100 mol% tungsten (MW100).

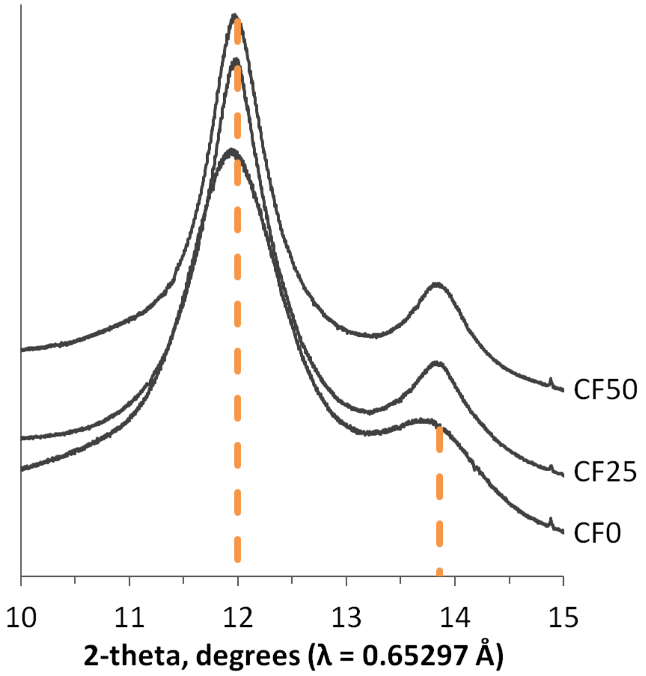

Figure S8 magnified SXRD pattern for samples containing Ce:Fe molar ratios of 100:0 (CF0), 75:25 (CF25) and 50:50 (CF50). The very slight (if any) peak shift from the control (100% CeO_2) sample to the iron-containing samples would suggest only a very small amount of Fe-doping in the CeO_2 phase.

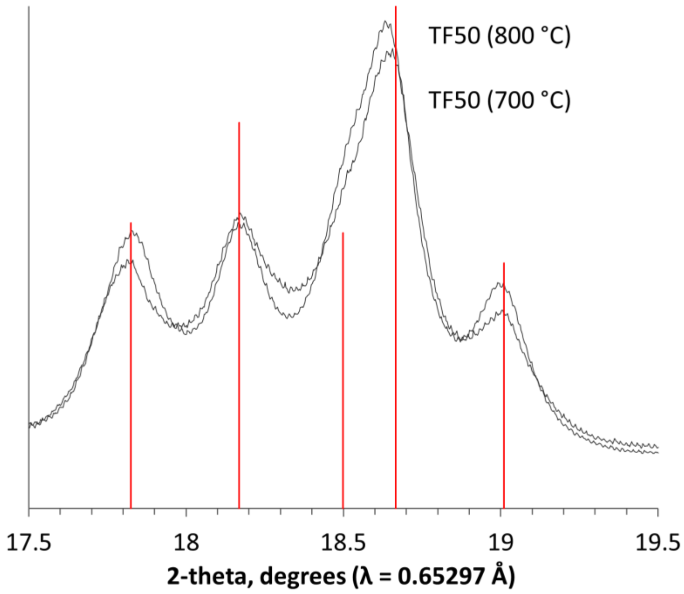

Figure S9 Magnified region for the PXRD pattern for sample TF50 at 700 °C and 800 °C showing very little (if any) peak shifting, suggesting a carbide rather than a carbonitride phase (Fe_3C). Given that Fe_3C is more thermodynamically stable than Fe_3N, if an intermediate carbonitride was formed in this system it would be reasonable to expect a peak shift with increasing temperature.[1]

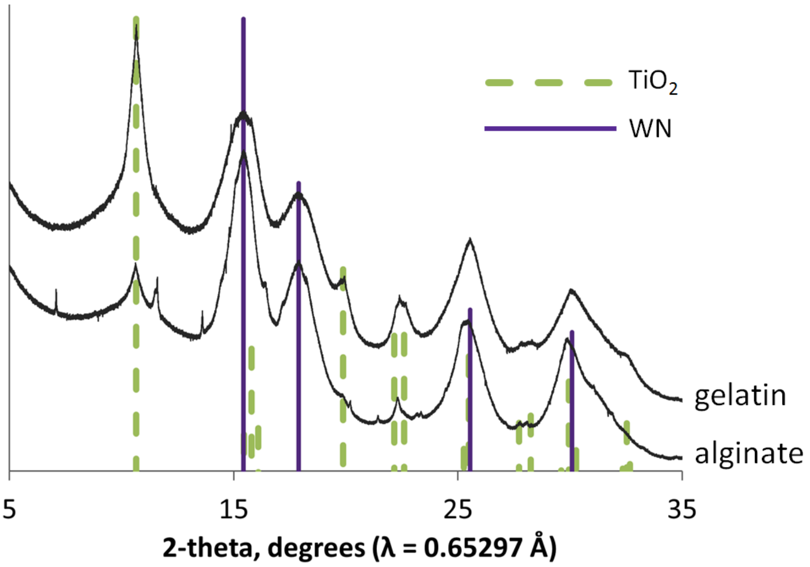

Figure S10 Samples of anatase/WN prepared using gelatin and alginate. (Alginate data is reproduced with permission from *Sci. Tech. Adv. Mater.* 2012, **13**, 035001). The samples prepared with alginate produced a mixture of TiO_2, WN and $Ti_xW_{1-x}N$ at high W-contents whereas the new preparation with a gelatin precursor produces distinct anatase and WN phases under the same heating conditions.

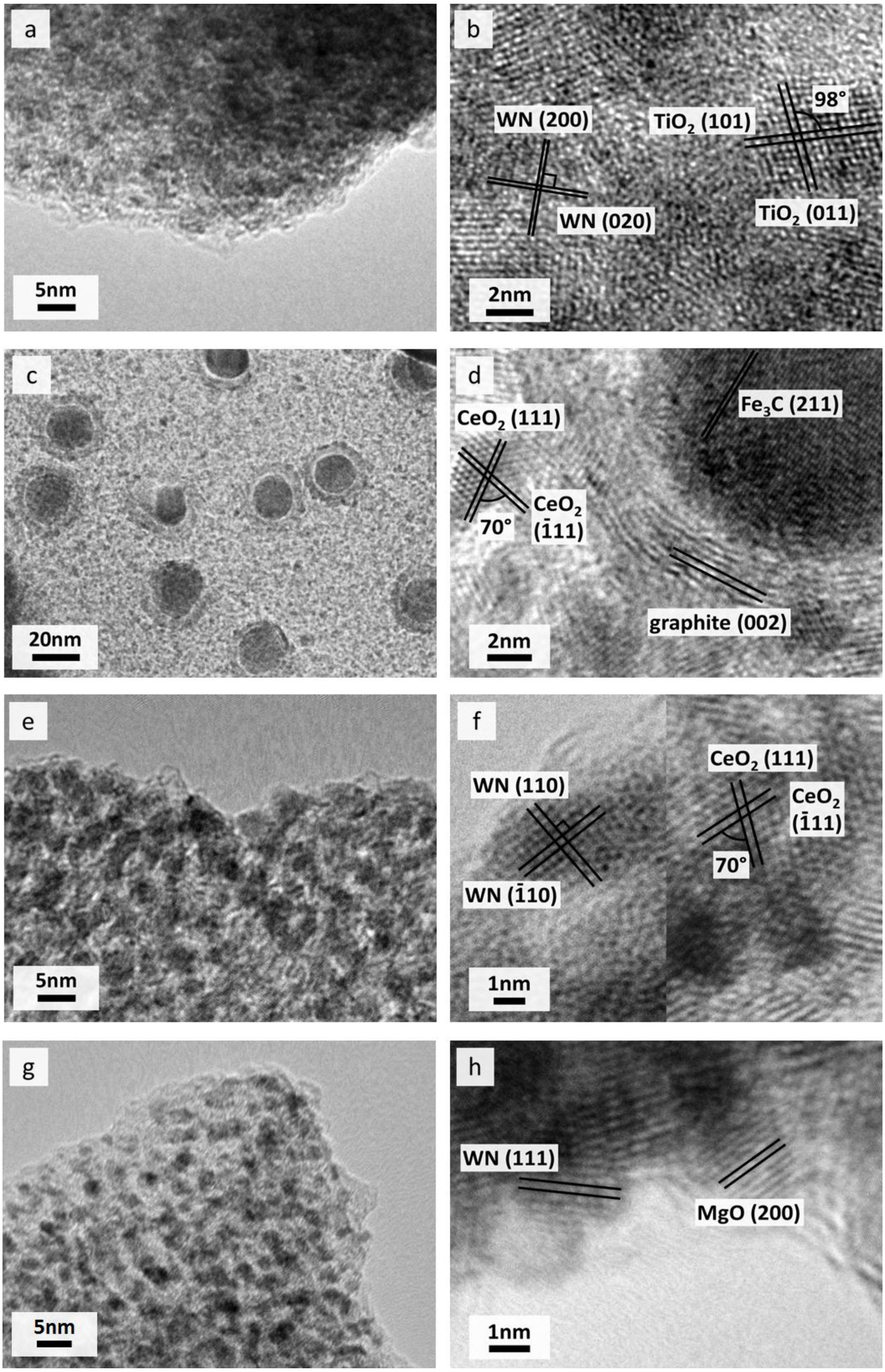

Figure S11 TEM/high-resolution TEM images showing sponge-like nanocomposites of a)/b) TiO_2/WN, c)/d) CeO_2/Fe_3C, e)/f) CeO_2/WN and g)/h) MgO/WN. Images show overlaid lines marking lattice plane spacings and interplanar angles corresponding to literature or calculated values.

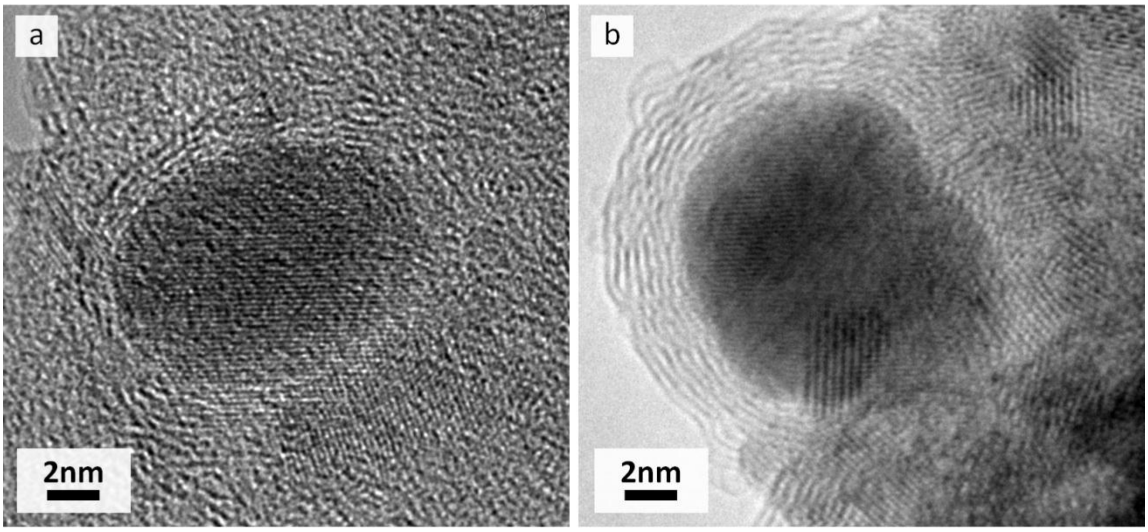

Figure S12 TEM images showing Fe_3C nanoparticles surrounded by ‘onion-like’ layers of graphite in a) TiO_2/Fe_3C and b) CeO_2/Fe_3C.

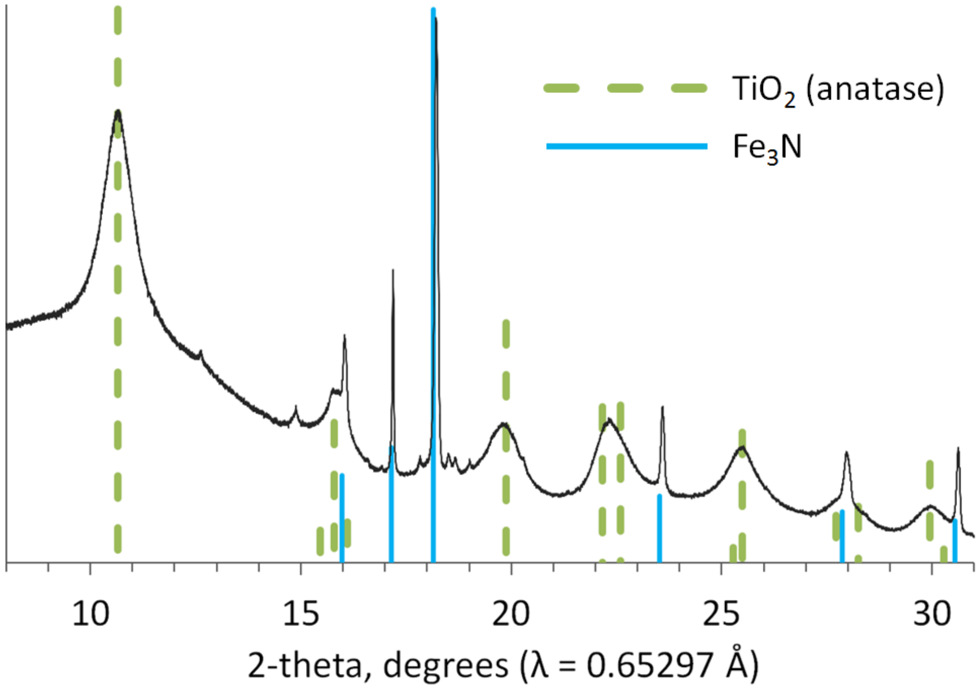

Figure S13 PXRD pattern of an anatase/Fe_3N sample produced using a reduced organic content in the precursor (10 g of 10% gelatin solution rather than 30g) and a lower heating temperature (700 °C).

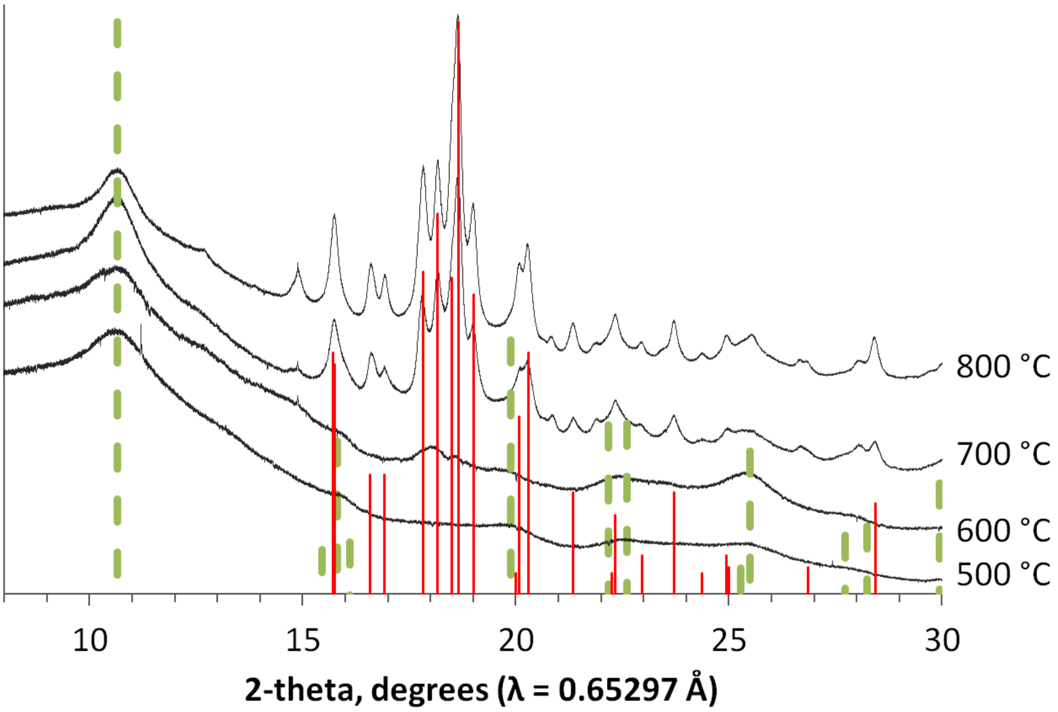

Figure S14 Samples prepared at various temperatures from a dried gelatin mixture containing iron nitrate and Ti(acac) at 50:50 molar ratio (TF50).

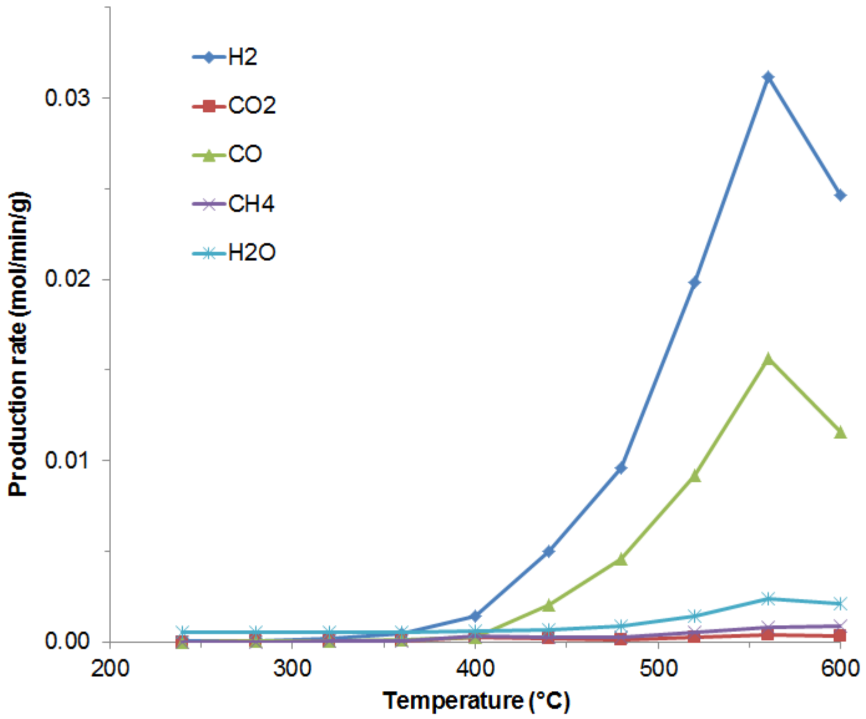

Figure S15 Molar production rate per gram of MF100 catalyst of hydrogen, carbon monoxide, and side products

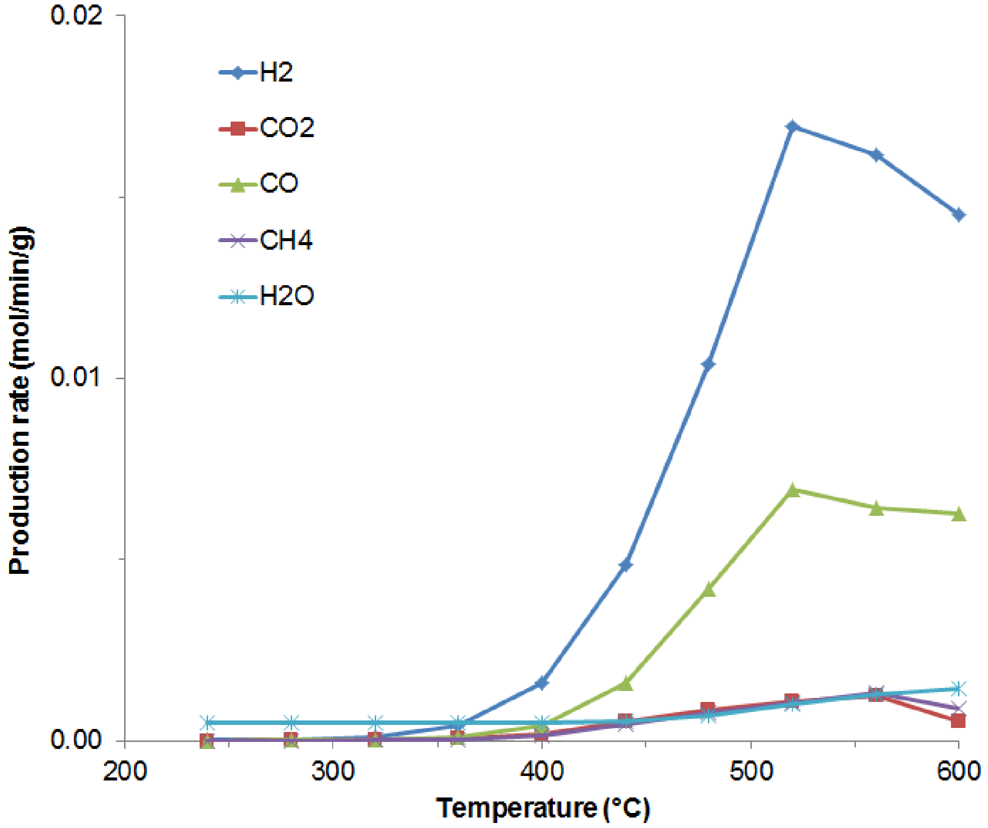

Figure S16 Molar production rate per gram of MF50 catalyst of hydrogen, carbon monoxide, and side products

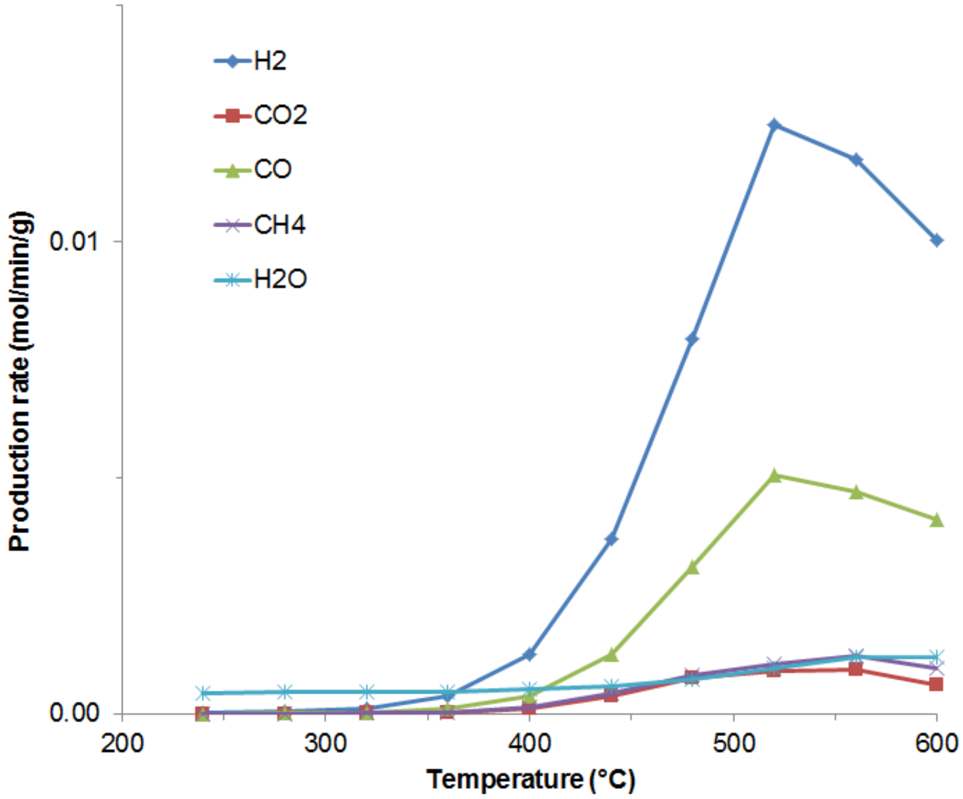

Figure S17 Molar production rate per gram of MF25 catalyst of hydrogen, carbon monoxide, and side products

Sample temperature (°C)	Feed of methanol *i.e.* total carbon input (mol/min)	Carbon-containing products (mol/min)	Unreacted methanol (mol/min)	Total carbon output (mol/min)	Error, %
240	1.00E-03	2.42E-05	1.23E-03	1.25E-03	-25.3
280	1.23E-03	2.54E-05	1.25E-03	1.27E-03	-3.0
320	1.27E-03	2.84E-05	1.26E-03	1.28E-03	-0.8
360	1.23E-03	3.48E-05	1.24E-03	1.27E-03	-3.2
400	1.23E-03	6.92E-05	1.20E-03	1.26E-03	-2.4
440	1.23E-03	1.52E-04	1.16E-03	1.32E-03	-7.3
480	1.23E-03	2.80E-04	9.46E-04	1.23E-03	0.7
520	1.27E-03	5.54E-04	6.86E-04	1.24E-03	2.0
560	1.25E-03	9.42E-04	3.44E-04	1.29E-03	-2.9
600	1.25E-03	7.20E-04	5.65E-04	1.28E-03	-2.8

Table S1 Carbon balance (% variation) for MF100 over stepwise Methanol decomposition. The very large variation for the initial measurement is thought to be due to instability of the methanol pump after start-up.

Sample temperature (°C)	**Feed of methanol *i.e.* total carbon input (mol/min)**	**Carbon-containing products (mol/min)**	**Unreacted methanol (mol/min)**	**Total carbon output (mol/min)**	**Error, %**
240	9.88E-04	2.49E-05	1.25E-03	1.28E-03	-29.6
280	1.25E-03	2.52E-05	1.23E-03	1.26E-03	-0.7
320	1.23E-03	2.66E-05	1.24E-03	1.27E-03	-2.6
360	1.25E-03	3.45E-05	1.24E-03	1.28E-03	-2.1
400	1.21E-03	6.35E-05	1.20E-03	1.26E-03	-4.4
440	1.25E-03	1.60E-04	1.09E-03	1.25E-03	0.0
480	1.21E-03	3.32E-04	8.47E-04	1.18E-03	2.6
520	1.25E-03	5.07E-04	7.18E-04	1.23E-03	2.0
560	1.24E-03	5.12E-04	6.96E-04	1.21E-03	2.7
600	1.23E-03	4.40E-04	7.80E-04	1.22E-03	1.1

Table S2 Carbon balance (% variation) for MF50 over stepwise Methanol decomposition. The very large variation for the initial measurement is thought to be due to instability of the methanol pump after start-up.

Sample temperature (°C)	**Feed of methanol *i.e.* total carbon input (mol/min)**	**Carbon-containing products (mol/min)**	**Unreacted methanol (mol/min)**	**Total carbon output (mol/min)**	**Error, %**
240	9.88E-04	0.00E+00	1.13E-03	1.13E-03	-14.0
280	1.23E-03	2.21E-05	1.15E-03	1.17E-03	4.5
320	1.23E-03	2.43E-05	1.15E-03	1.18E-03	4.5
360	1.24E-03	3.01E-05	1.15E-03	1.18E-03	5.0
400	1.20E-03	5.42E-05	1.12E-03	1.17E-03	1.9
440	1.26E-03	1.25E-04	1.03E-03	1.16E-03	7.9
480	1.21E-03	2.62E-04	9.22E-04	1.18E-03	2.3
520	1.23E-03	3.81E-04	7.70E-04	1.15E-03	6.8
560	1.20E-03	3.76E-04	7.50E-04	1.13E-03	5.9
600	1.26E-03	3.22E-04	8.09E-04	1.13E-03	10.1

Table S3 Carbon balance (% variation) for MF25 over stepwise Methanol decomposition. The very large variation for the initial measurement is thought to be due to instability of the methanol pump after start-up.

	H_2/CO ratio		
Temperature	**MF100**	**MF50**	**MF25**
280	8.8	6.8	4.643
320	6.3	4.9	3.552
360	5.9	4.3	3.373
400	5.3	3.9	3.296
440	2.4	3.0	2.925
480	2.1	2.5	2.542
520	2.2	2.4	2.473
560	2.0	2.5	2.501
600	2.1	2.3	2.45

Table S4 H_2/CO ratios with increasing temperature during methanol decomposition for samples MF100, MF50 and MF25.

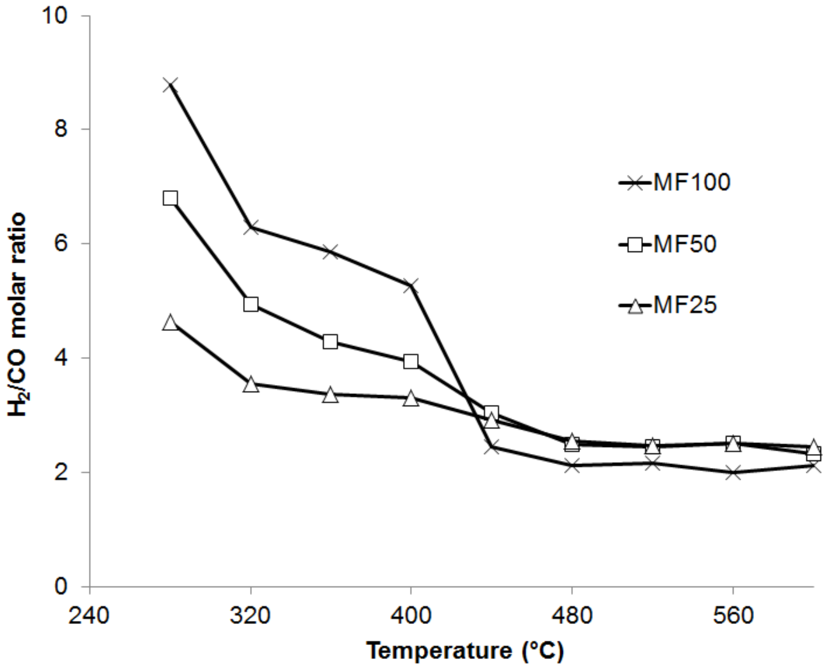

Figure S18 Chart of H_2/CO molar ratio with increasing reaction temperature during stepwise methanol decomposition.

Supplementary Experimental Information

Precursor solutions:

A Ti(acac) stock solution was prepared by mixing titanium ethoxide (12.5 g), acetylacetone (5 g) and ethanol (20 g) to give a homogeneous yellow solution.
A magnesium nitrate stock solution was prepared by dissolving $Mg(NO_3)_2.6H_2O$ (1 g) in deionized water to give a total volume of 10 ml
A cerium nitrate stock solution was prepared by dissolving $Ce(NO_3)_3.6H_2O$ (1 g) in deionized water to give a total volume of 10 ml
An iron nitrate stock solution was prepared by dissolving $Fe(NO_3)_3.9H_2O$ (1 g) in deionized water to give a total volume of 10 ml
An ammonium metatungstate stock solution was prepared by dissolving $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ (1 g) in deionized water to give a total volume of 10 ml

A gelatin solution was prepared by dissolving gelatin (Sigma Aldrich Type A Porcine Gelatin G2500, 10 g) in boiling water (90 g) to give a 10% by mass solution.

Sample preparation

TF, MF, MW, CF and CW samples were prepared by premixing aliquots of the metal stock solutions as listed in the following table then quickly adding the mixture to a hot and rapidly stirring beaker of gelatin (30 g). This resulted in a mixture of 0.01 total moles of metal to 3 g of gelatin polymer for each sample.

TW samples were prepared by premixing ammonium tungstate with hot gelatin, then adding Ti(acac) stock to the rapidly stirring mixture.

All samples were left in open beakers in air at 80 °C to dry. Depending on the metals, some of the samples spontaneously expanded during the final stages of drying to give a sponge-like structure.

Following drying, the samples were placed in capped crucibles and heated at 10 $°Cmin^{-1}$ under a stream of nitrogen in a muffle furnace. Iron-containing samples were heated to 800 °C, held for 5 minutes then cooled to room temperature under nitrogen. Tungsten-containing samples were heated to 900 °C, held for 5 minutes then cooled to room temperature under nitrogen.

Sample code	Molar ratio Mg:Fe	Volume $Mg(NO_3)_2$ (ml)	Volume $Fe(NO_3)_3$ (ml)
MF0	100:0	25.60	0.00
MF25	75:25	19.20	10.10
MF50	50:50	12.80	20.20
MF100	0:100	0.00	40.40

Sample code	Molar ratio Mg:W	Volume $Mg(NO_3)_2$ (ml)	Volume $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ (ml)
MW0	100:0	25.60	0.00
MW25	75:25	19.20	5.36
MW50	50:50	12.80	10.73
MW100	0:100	0.00	21.45

Sample code	Molar ratio Ti:Fe	Volume Ti(acac) stock (ml)	Volume $Fe(NO_3)_3$ (ml)
TF0	100:0	7.02	0.00
TF25	75:25	5.27	10.10
TF50	50:50	3.51	20.20
TF100	0:100	0.00	40.40

Sample code	Molar ratio Ti:W	Volume Ti(acac) stock (ml)	Volume $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ (ml)
TW0	100:0	7.02	0.00
TW25	75:25	5.27	5.36
TW50	50:50	3.51	10.73
TW100	0:100	0.00	21.45

Sample code	Molar ratio Ce:Fe	Volume $Ce(NO_3)_3$ (ml)	Volume $Fe(NO_3)_3$ (ml)
CF0	100:0	43.40	0.00
CF25	75:25	32.55	10.10
CF50	50:50	21.70	20.20
CF100	0:100	0.00	40.40

Sample code	Molar ratio Ce:W	Volume $Ce(NO_3)_3$ (ml)	Volume $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ (ml)
CW0	100:0	43.40	0.00
CW25	75:25	32.55	5.36
CW50	50:50	21.70	10.73
CW100	0:100	0.00	21.45

Table S5 Full list of sample preparation details.

Catalysis

Catalytic experiments were carried out over the powder samples in a conventional fixed-bed flow reactor composed of a quartz tube, in a process similar to that described previously.[2] Powder samples (0.05 g) were supported in the quartz tube between plugs of glass wool. Before measurement, the samples were reduced at 513 K for 1 h in flowing hydrogen. After the hydrogen was flushed with nitrogen, methanol was introduced to the quartz tube at a feed rate of 50 μl min^{-1}. Methanol was fully evaporated in a thermal evaporator at 423 K before being introduced to the quartz tube. The catalytic properties of the powder samples were evaluated in a temperature range of 513–873 K at 40 K intervals by measuring the outlet composition of gaseous products with a gas chromatograph (GL Science) and the total flow rate of outlet gases with a soap bubble meter. We calculated the production rates of the gaseous products by the following equation:

$$R_{\mathrm{H_2}} = \frac{C_{\mathrm{H_2}} \times F_{\mathrm{total}}}{A}$$

where R_{H2} is the production rate of H_2; C_{H2} is the volume fraction of H_2 in total outlet gases excluding gasified species, CH_3OH and H_2O; F_{total} is the flow rate of total outlet gases (mol h^{-1})

excluding gasified species; and *A* is the mass of the sample (g). The production rates of CO,CH_4, and CO_2 were obtained using a similar calculation. The production rate of H_2O was calculated based on the ratio of volume fraction of H_2 to that of gasified H_2O in total outlet gases.

X-ray pattern referencing

XRD reference patterns used for analysis were: TiO_2 (ICDD 01-070-7348), CeO_2 (ICDD 00-043-1002), MgO (ICDD 01-089-7746), Fe_3C (ICDD 01-089-2722) and WN (ICDD 01-075-1012)

Carbon balance

The carbon balances were determined as described previously[2]

---

[1] *Proc. R. Soc. Lond. A* 1948 **195**, 41-55

[2] *Journal of Catalysis*, 2006, **243**, 99–107