Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Robust mesoporous bimetallic yolk-shell catalysts for chemical CO_2 upgrading via dry reforming of methane

Cameron-Alexander Hurd Price[a], Laura Pastor-Pérez[a,b], Tomas Ramirez Reina*[a] and Jian Liu*[a,c]

Synthesis

All chemicals were purchased from Sigma-Aldrich, unless otherwise stated, and were used without further purification or treatment.

The Ni/ZnO@*m*-SiO_2 yolk shell material was prepared as follows.

Synthesis of ZIF-8 9.4mM of Zinc Nitrate was added to 60 ml methanol. A second solution was produced by the addition of 0.04M 2-methylimidazole to 40 ml methanol. The two solutions were combined and left to stir for 24 hours at ambient temperature. The resulting suspension was then centrifuged and washed with methanol before being dried overnight.

Synthesis of ZIF-8-Ni 0.244g of Nickel Acetate was dissolved in 50 ml deionised (DI) water to produce a 0.02M solution. 0.2g ZIF-8 was then added under stirring and left for 24 hours. This suspension was then centrifuged and washed with DI water before being dried overnight.

Synthesis of ZnO-Ni@m-SiO_2 Yolk Shells 5.48mM Centrimonium Bromide was dissolved in 40 ml DI water and 16 ml Ethanol, before 0.2 ml 25% ammonia solution was added under stirring for 30 minutes. Following which, 0.2g ZIF-8-Ni was added and left to stir for another 30 minutes. 600 µl tetraethyl orthosilicate was added dropwise and left to stir for 24 hours. Finally, the reaction solution was decanted into Teflon lined autoclaves and heated statically to 100°C for 24 hours before the solid product was recovered by centrifugation and dried for 24 hours. The resulting catalysts has a Ni loading of ca. 15 wt. %

Synthesis of Ni/Al_2O_3 & Ni/SiO_2-Al_2O_3 These materials were prepared using standard wet impregnation methodology and the Ni loading was set to be comparable to that of the yolk-shell catalysts (ca. 15 wt.%). 1.719mM $Ni(NO_3)_2.6H_2O$ was dissolved in excess ethanol under agitation before 4.5g Al_2O_3 or SiO_2-Al_2O_3 (SIRALOX® 30/280, SASOL), respectively, was added to the solution. The solution was left to stir for 1 hour before being transferred into a 500ml round bottomed flask and recovered using a rotary evaporator. The resulting powder was dried at 100°C overnight before being calcined in a muffle furnace at 500°C, 2°C/min in air.

Catalytic Activity

The dry reforming of methane was undertaken in a quartz tube (10 mm ID) at atmospheric pressure with 100 mg catalyst supported on a bed of quartz wool using a WHSV of 30,000 ml(gh)$^{-1}$. The percentage content of CO_2, CH_4, H_2 and CO of the gas flow was determined by an ABB on-line analyser (ABB AO2020) equipped with both IR and TCD detectors. Pre-treatment of the samples occurred at 850°C, 20% H_2/N_2 for 1 hour.

For the temperature screening reaction, the operating temperature was varied from 500-850°C using a constant reactant flow of 50 ml/min (CH_4:CO_2:N_2 / 1:1:3). 100 mg of material was used to achieve a weight hourly space velocity of 30,000 ml(g h)$^{-1}$.

For the stability test, the temperature was maintained at 850°C under the same flow conditions and weight hourly space velocity as the temperature screening experiments.

The standard deviation was calculated for the conversion values of our reactants and was found to be within 5% error. All equilibria values for the DRM reaction were achieved with ChemStations' ChemCad software package over a range of temperatures. The Soave-Redlich-Kwong equation of state was used in a Gibbs reactor and material flows into the reactor are identical to those intended to be used experimentally.

Catalysts Characterisation

X-Ray Diffraction analysis (XRD) analysis was carried out at room temperature on an X'Pert Pro PANalytical diffractometer. The patterns were obtained using Cu Kα radiation (30 mA, 40 kV) with a 2Θ-range of 10–90° and a step size of 0.05° with a step time of 160s.

Raman spectroscopy measurements were performed on a Thermo Scientific DXR Raman Microscope using a green laser (λ = 532 nm, maximum power 10 mW) with a spot diameter of 0.7 µm and a pinhole aperture of 50 µm. A diffraction grating of 900 grooves mm^{-1}, a CCD detector and a 50× objective were used.

TEM images were taken with a JEOL electron microscope (model JEM-2010) working at 200 kV. It was equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in ethanol and placed on copper grids with a holey-carbon film support.

Scanning electron microscope (SEM) imagery was carried out on a JEOL 7100f equipped with an Energy Dispersive X-ray Spectroscope (EDS) analyser (Oxford Link).

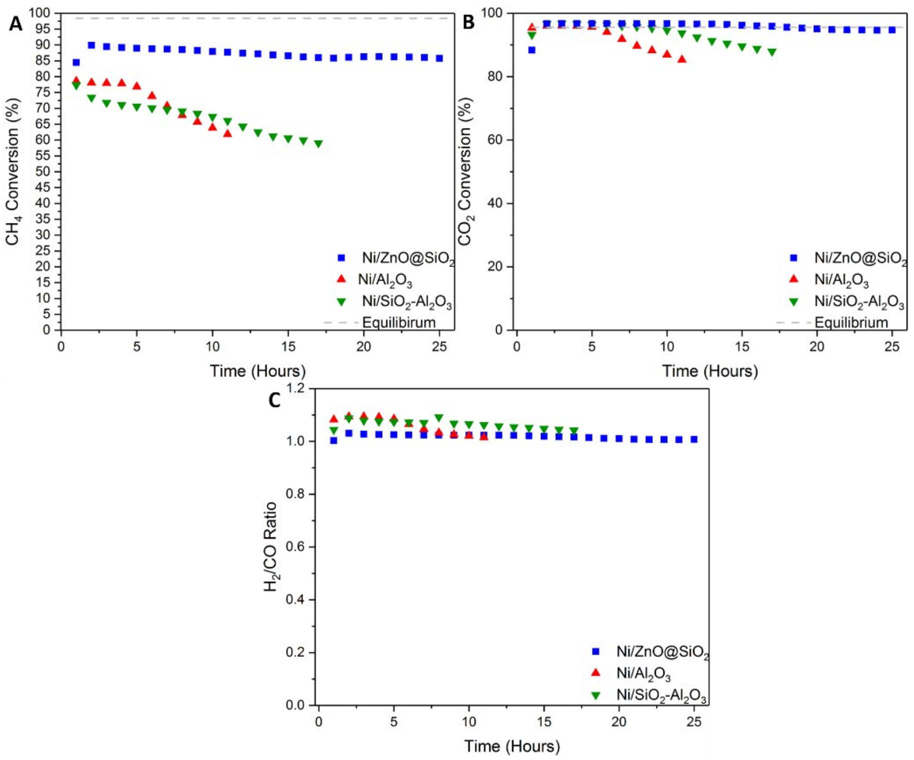

Figure S1: 25 hours stability data for our reported material against Ni/Al_2O_3 and Ni/SiO_2-Al_2O_3 concerning A) CH_4 conversion B) CO_2 conversion and C) H_2/CO ratio.

The H_2/CO ratios displayed by the comparative material in Figure S1 can be noted to exceed the theoretical equilibria are attributed to methane decomposition at high temperatures and the associated negative correlation, as coke formation on the catalyst.

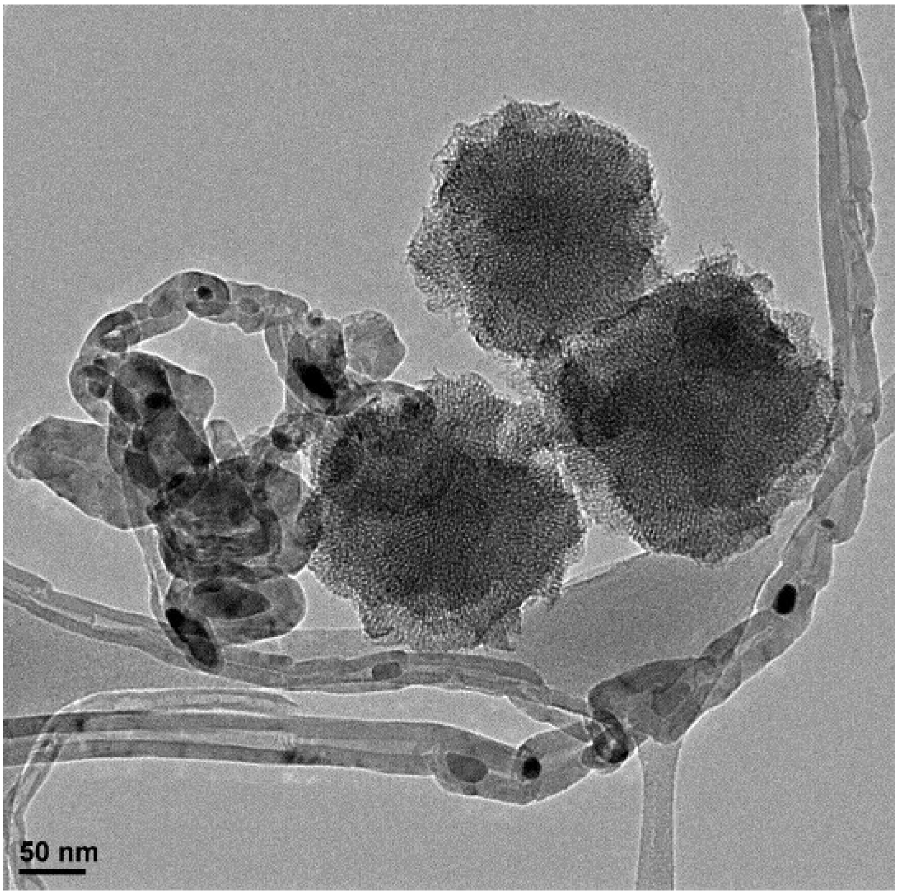

Figure S2: Carbon nanotube formation clearly enclosing the Ni/ZnO ‘free’ cores (black spots) while leaving the larger yolk shells free of carbon.

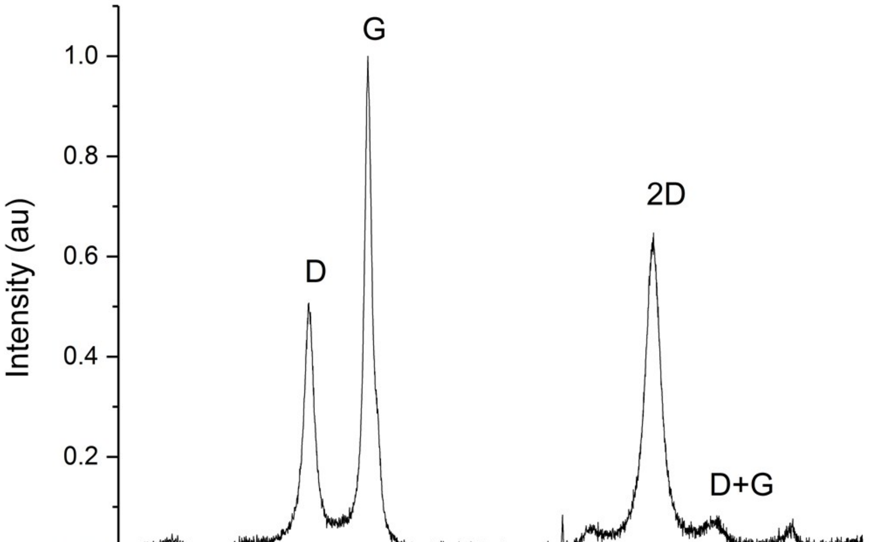

Figure S3: Raman of the post reaction sample, clearly displaying the D, G, 2D and D+G bands for the formed carbon. The I_D/I_G ratio of 0.54 clearly indicates the carbon formed is very graphitic.

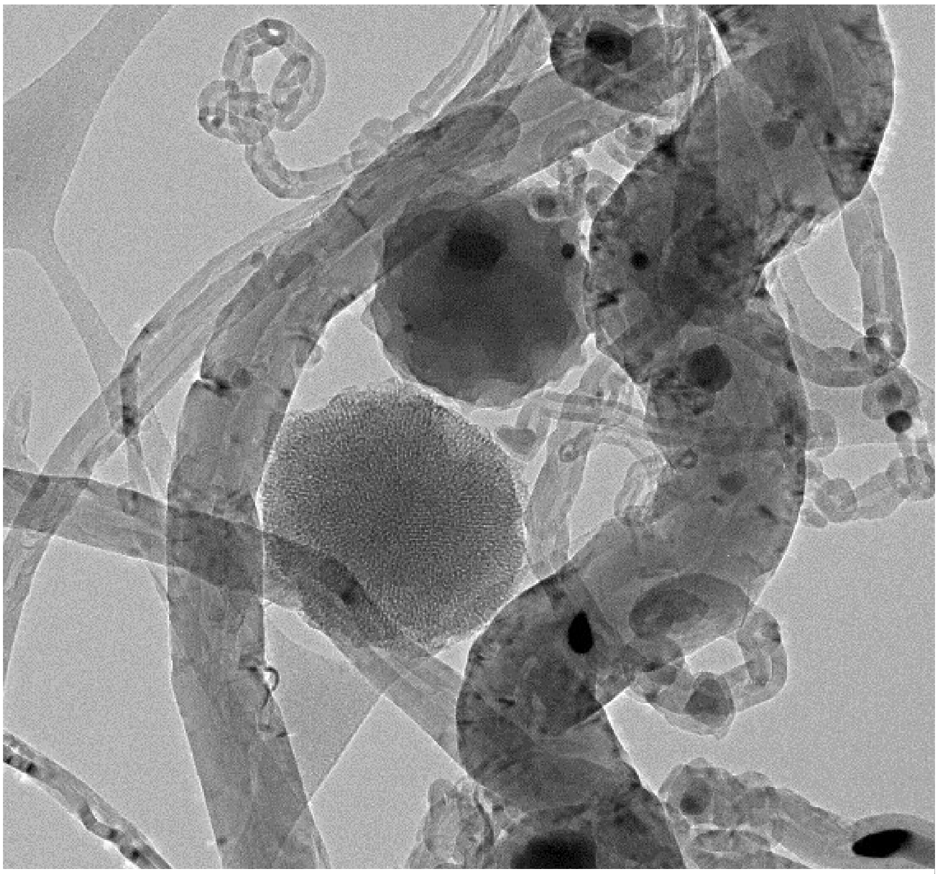

Figure S4: The formation of carbon nanotubes around unencapsulated Ni/ZnO Particles (black spots) can be seen here to surround the yolk shell particles, preventing reactant access.

Table S1 Comparative table detailing the present work catalyst against a number of materials recently reported in the literature

Material	Temperature (^{o}C)	WHSV (ml(g_{cat}h)$^{-1}$)	CH_4 Conversion after 10 hours (%)	CH_4 Conversion after 50 hours (%)	Ref
ZnO/Ni@SiO_2	850	30,000	88	78	This work
Ni/Al_2O_3	800	36,000	69	43	1
Ni-Mo_2C/La_2O_3	800	12,000	55	65	2
SnNi/Ce-Al	800	60,000	51	13	3
NiMgAl	800	80,000	83	-	4
Ni@SiO_2	750	36,000	82	-	5
Ni-Co/SiO_2	700	72,000	75	-	6
Ni-Mg@SiO_2	750	60,000	87	85	7
Ni/SBA-15	700	36,000	75	75	8

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