UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

$Ni@SiO_2$ vs $SiO_2@Ni$ Catalyst: The effect of catalyst/support orientation on performance

Lois Milner, Martin Khzouz, Robert Steinberger-Wilckens

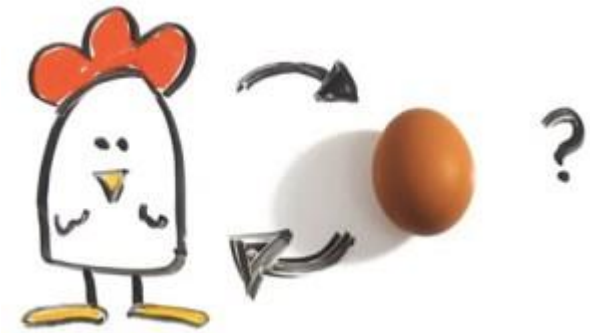
CDT in Fuel Cells and their Fuels

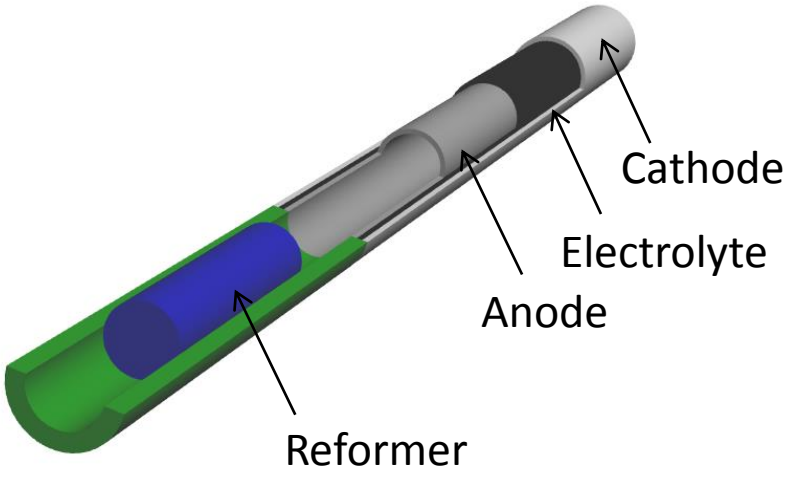
FCH_2, NEC Birmingham

14th March 2018

EPSRC Engineering and Physical Sciences Research Council

Application of the catalyst





Methane reforming

- Steam Reforming

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

- Dry Reforming

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$$

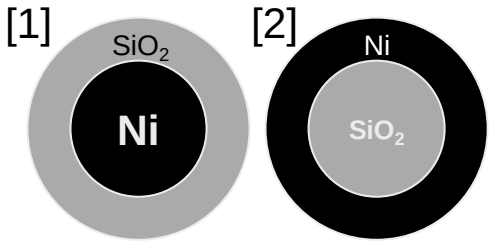
- Partial Oxidation

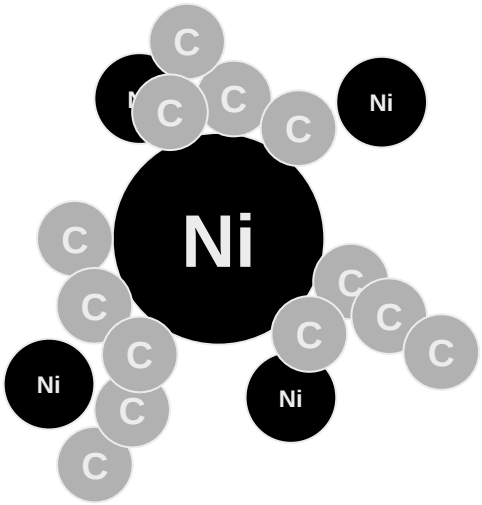
$$CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO$$

Why the interest in Ni/SiO_2

$$CH_{4\,(g)} \rightarrow C_s + 2H_2$$

$$2CO \rightarrow CO_2 + C_s$$





A good support can:

- Maintain catalyst dispersion through strong catalyst-support interactions
- Be basic
- Provide mechanical and thermal stability
- Provide a pathway for electron transfer between reagents
- Physically suppress coke formation
- Decrease the amount of active metal needed to provide a high surface area

[1] L. Li, S. He, Y. Song, J. Zhao, W. Ji, C.-T. Au, J. Catal. 288 (2012)
[2] A.J. Majewski, J. Wood, W. Bujalski, Int. J. Hydrogen Energy. 38 (2013) 14531–14541.

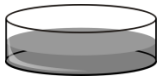
Synthesis

PEG, NaOH and DI water sln.

$Ni(NO_3)_2.6H_2O$ in DI water

Stir 1 hour

Centrifuge Wash in DI + EtOH



NiO

Calcine at 350°C for 2 hours

PVP and EtOH

ammonia

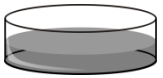
Stir for 12 hours

Sonicate 30 min

TEOS + EtOH sln.

Sonicate 1 hour

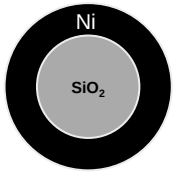
Centrifuge Wash in DI + EtOH



Dry at 80°C overnight

L. Li, S. He, Y. Song, J. Zhao, W. Ji, C.-T. Au, J. Catal. 288 (2012)

D. Qi, C. Lin, H. Zhao, H. Liu, T. Lü, J. Dispers. Sci. Technol. 38 (2016) 70–74.
A.J. Majewski, J. Wood, W. Bujalski, Int. J. Hydrogen Energy. 38 (2013) 14531–14541.

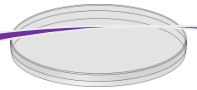


EtOH, TEOS, DI water and Ammonia

Stir 48 hour at 25°C

Heat to [illegible]°C, stir [illegible] hrs

Dry at 60°C overnight



SiO_2

Centrifuge Wash in DI

$Ni(NO_3)_2.6H_2O$ + DI water

Sonicate 30 min

Heat to 95°C

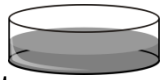
Urea

Stir 4 hours

Centrifuge Wash in DI

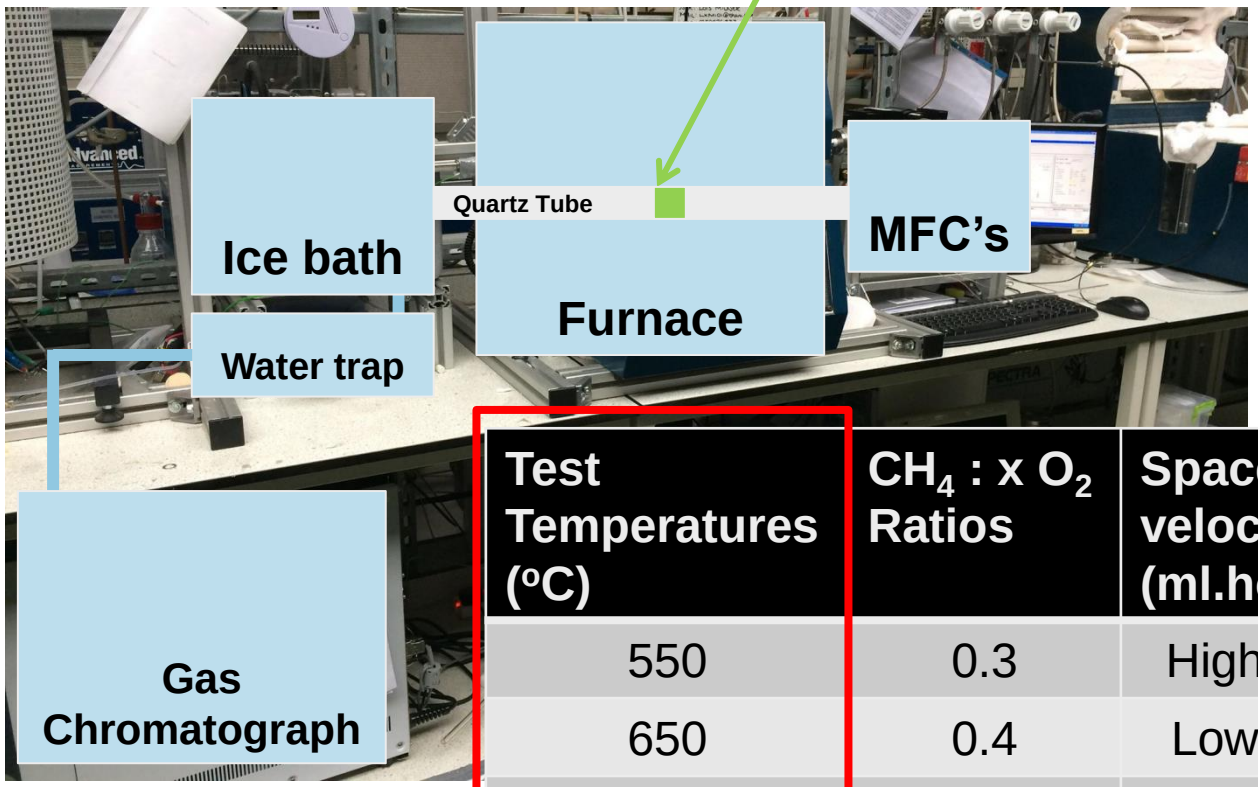
Dry at 80°C overnight

Calcine at 700°C for 4 hours



UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

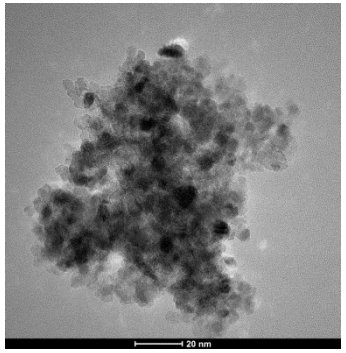
Testing Activity

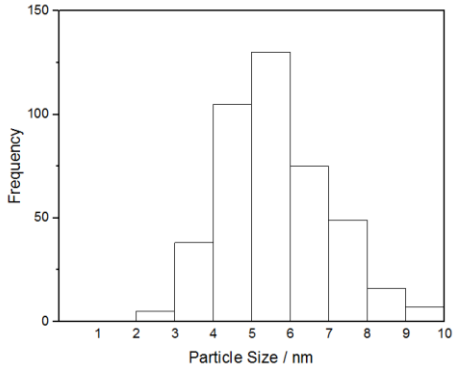


Test Temperatures (°C)	CH_4 : x O_2 Ratios	Space velocities (ml.hour $^{-1}$.g^{-1})
550	0.3	High (80640)
650	0.4	Low (16128)
750	0.5	
850	0.6	
950	0.7	

Microscopy and particle sizes

Ni

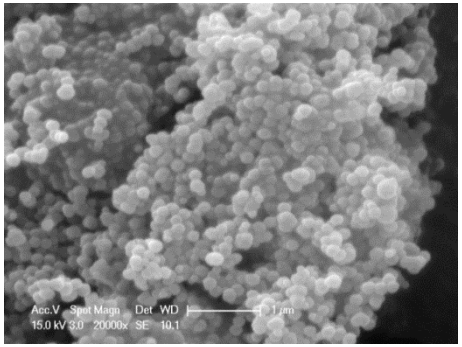


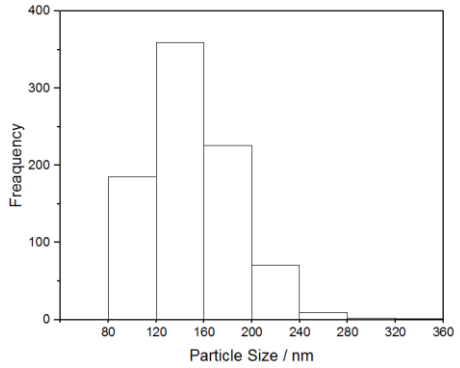


Mean core size:

5.6nm

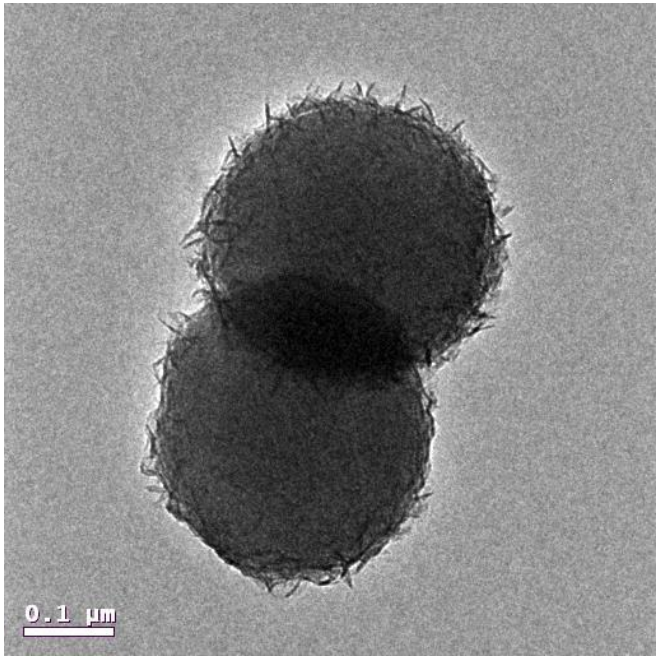
SiO_2





151.5nm

Nickel Phyllosilicate



Catalysis Science & Technology

COMMUNICATION

View Article Online
View Journal | View Issue

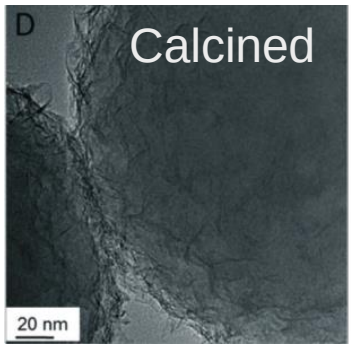
Ammonia-assisted synthesis towards a phyllosilicate-derived highly-dispersed and long-lived Ni/SiO_2 catalyst†

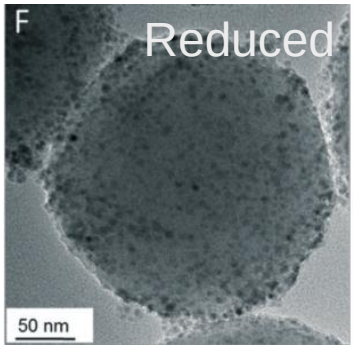
Cite this: *Catal. Sci. Technol.*, 2015, 5, 5095

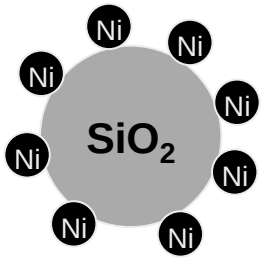
Received 18th August 2015,
Accepted 15th October 2015

DOI: 10.1039/c5cy01361e

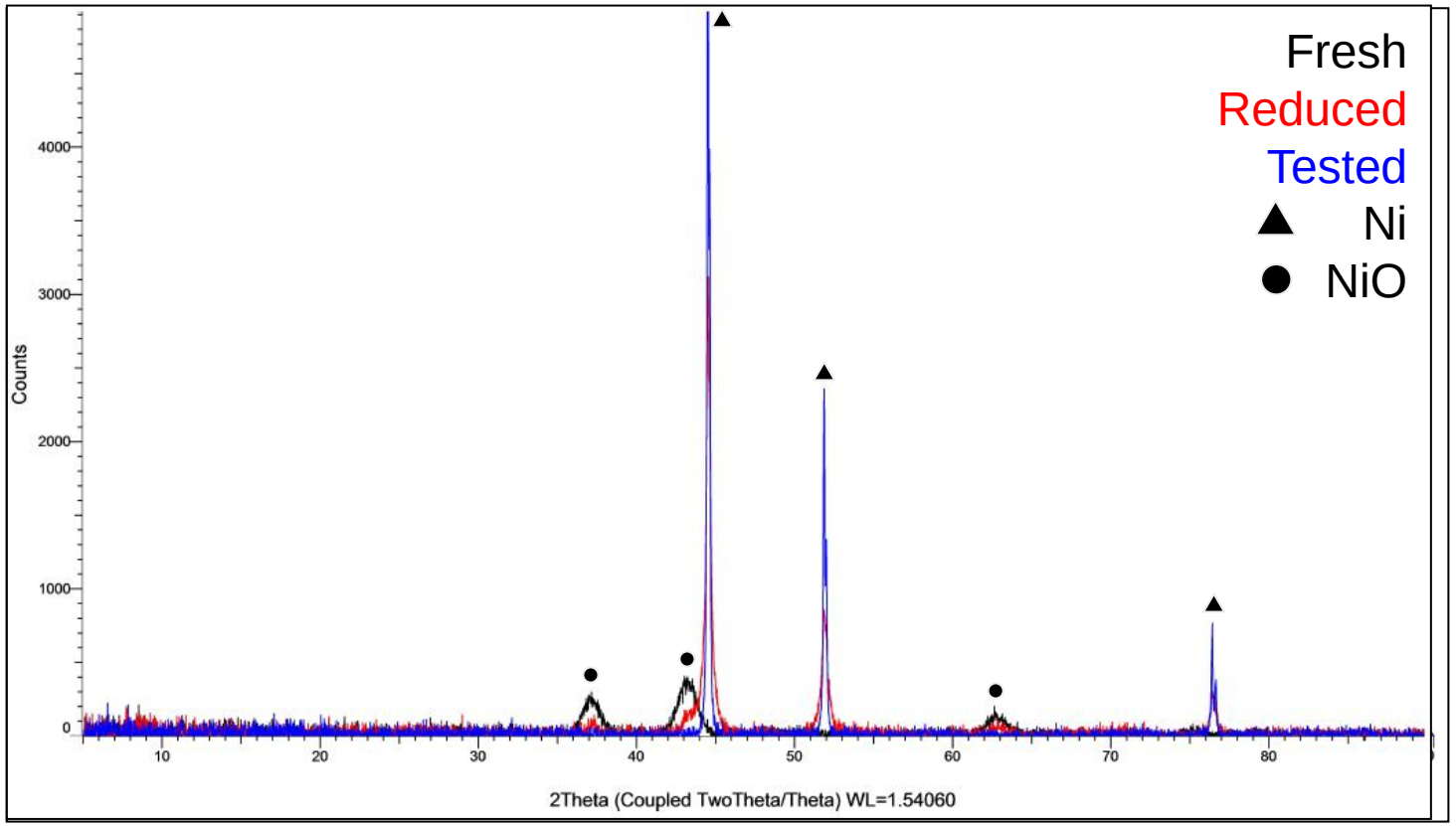
Meihua Yang, Peng Jin, Yinrui Fan, Chuanjing Huang,* Nuowei Zhang, Weizheng Weng, Mingshu Chen and Huilin Wan*



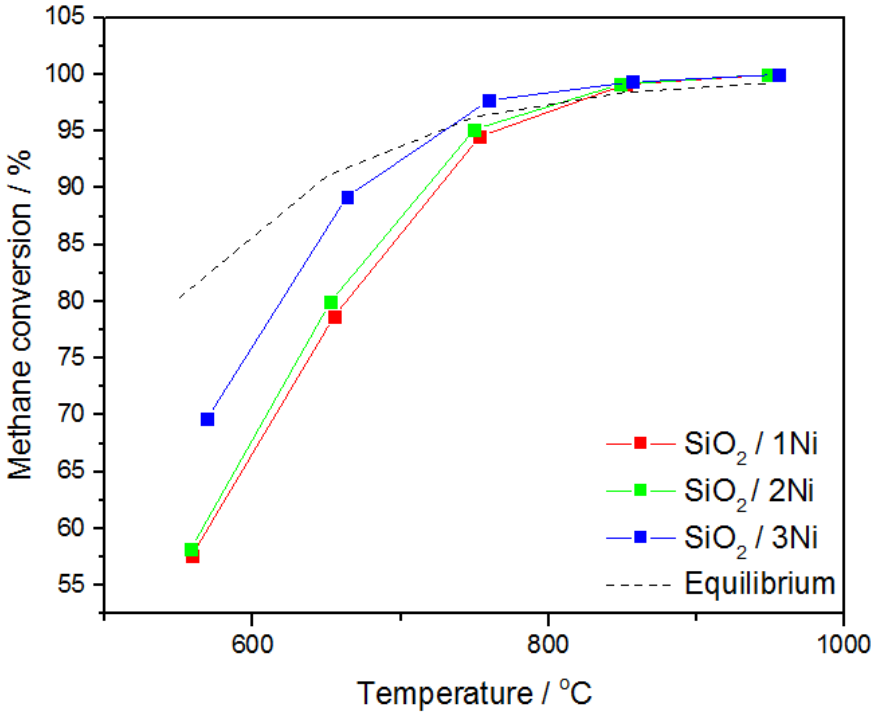


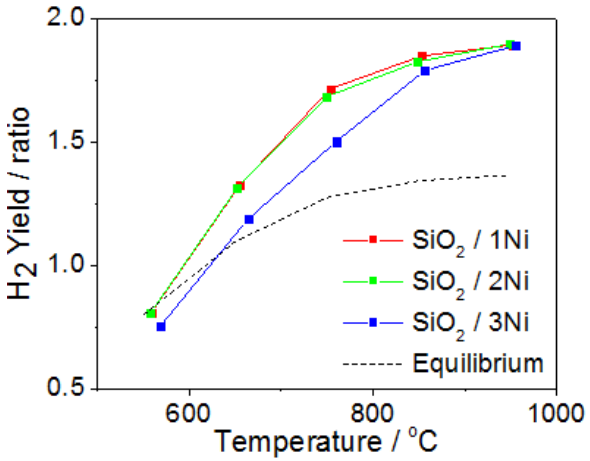


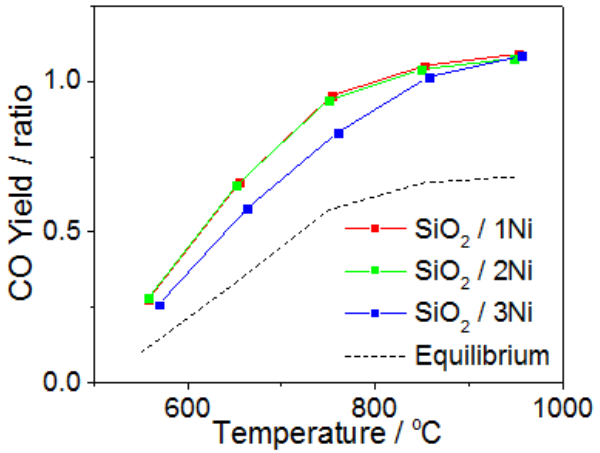
Bare Ni vs Ni@SiO_2

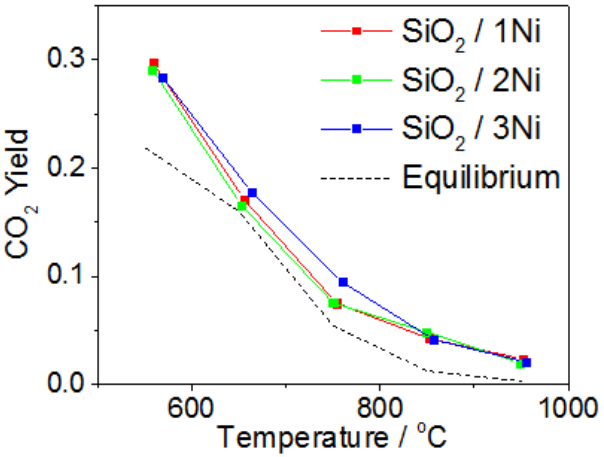


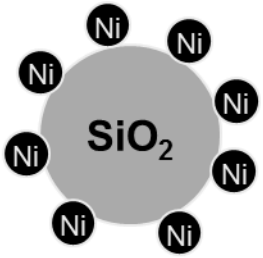
SiO_2 / Ni


Methane conversion / %
Temperature / °C
SiO2 / 1Ni
SiO2 / 2Ni
SiO2 / 3Ni
Equilibrium

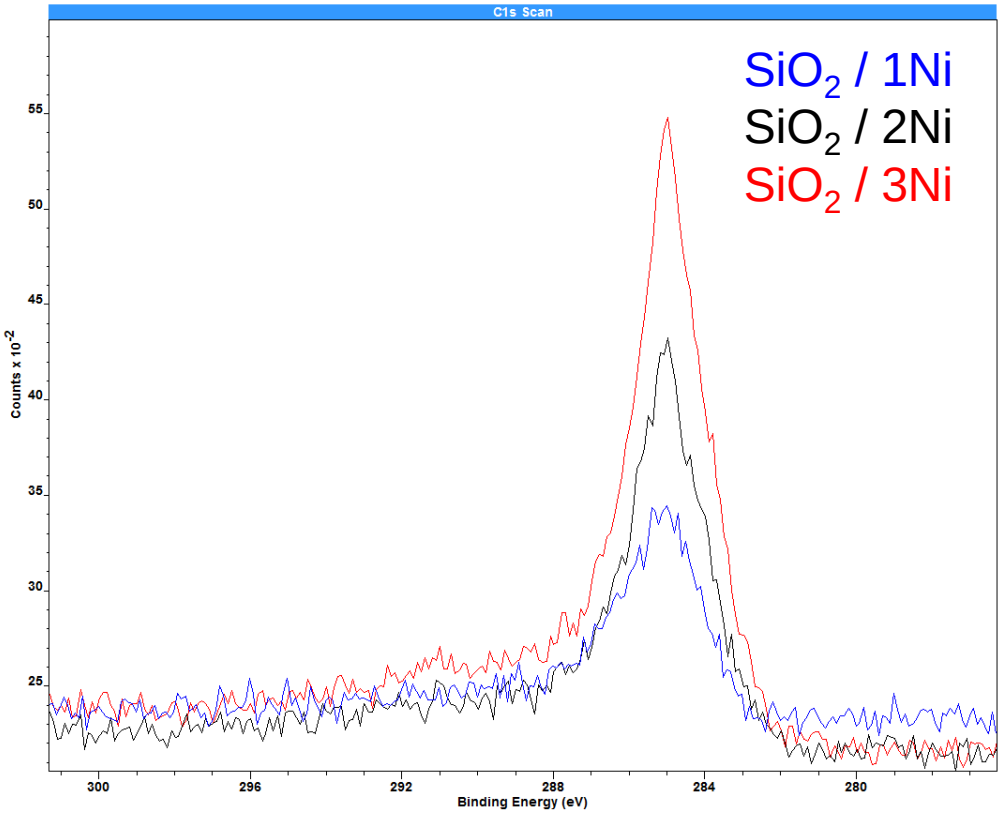

H2 Yield / ratio
Temperature / °C
SiO2 / 1Ni
SiO2 / 2Ni
SiO2 / 3Ni
Equilibrium


CO Yield / ratio
Temperature / °C
SiO2 / 1Ni
SiO2 / 2Ni
SiO2 / 3Ni
Equilibrium

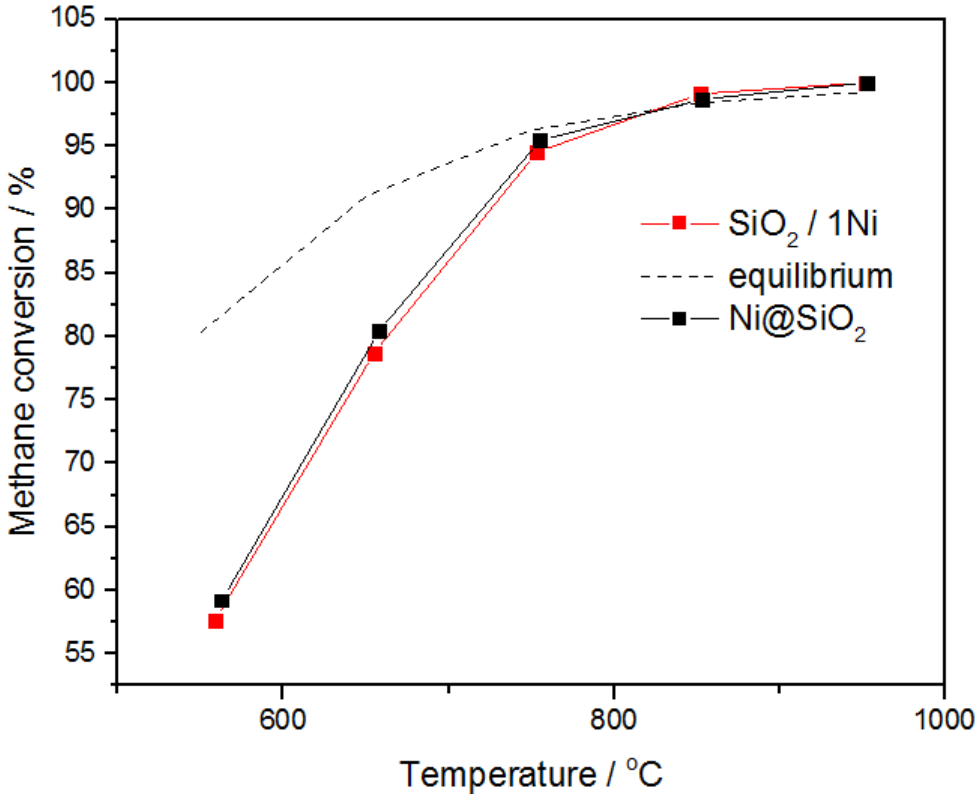

CO2 Yield
Temperature / °C
SiO2 / 1Ni
SiO2 / 2Ni
SiO2 / 3Ni
Equilibrium

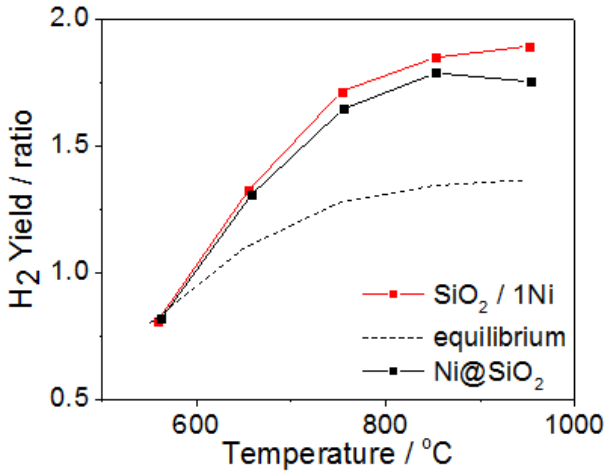

Ni
SiO2

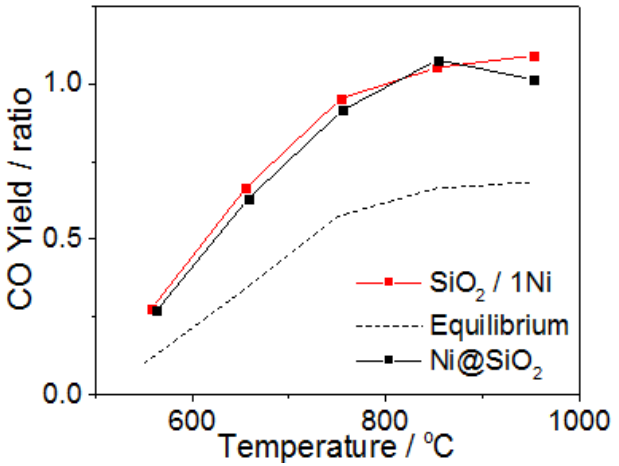
C 1s Peak – Tested Catalysts

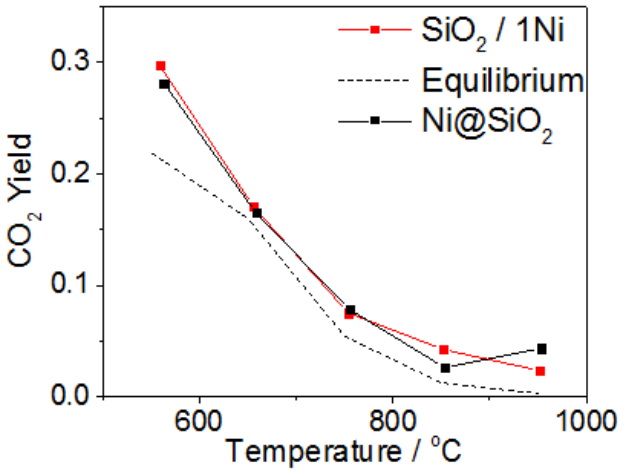


SiO2 / 1Ni vs Ni@SiO2

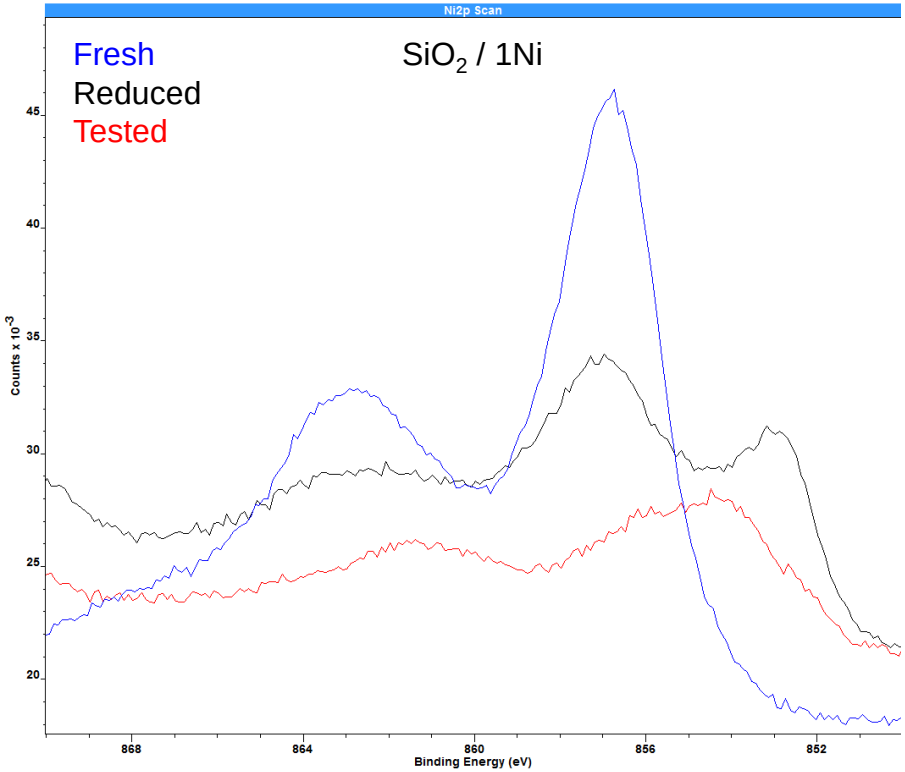


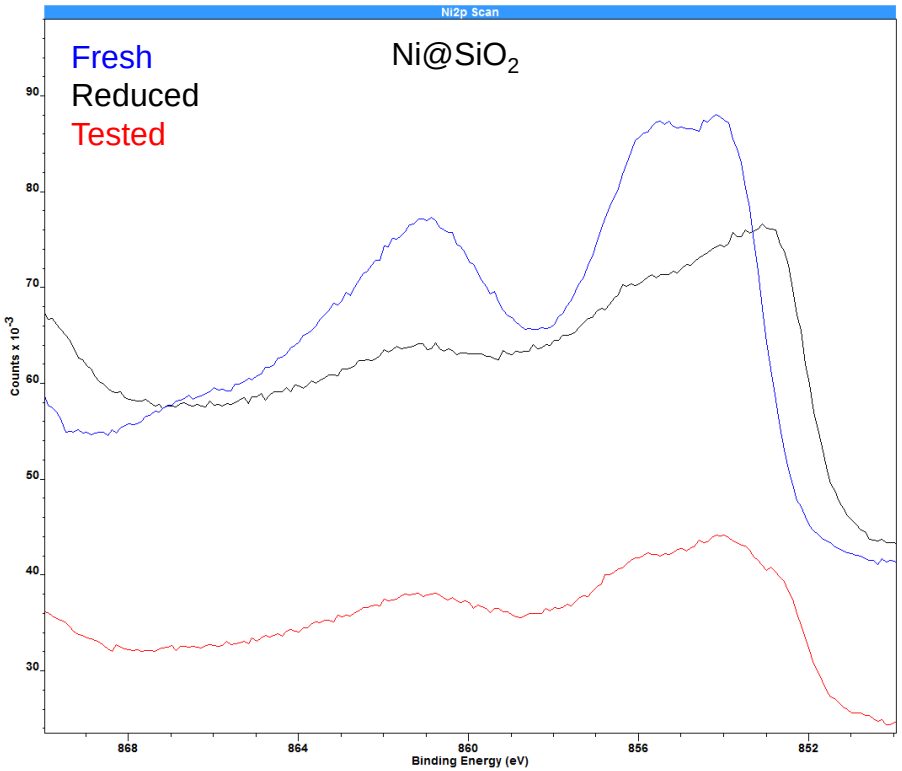




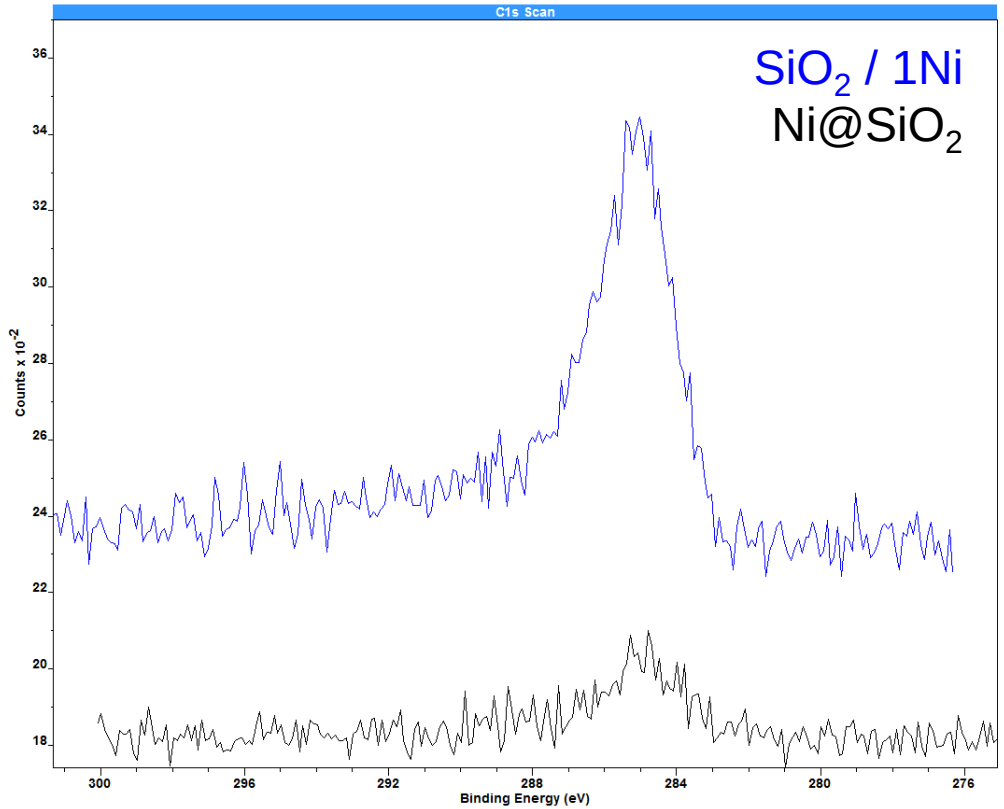


Ni 2p Peak

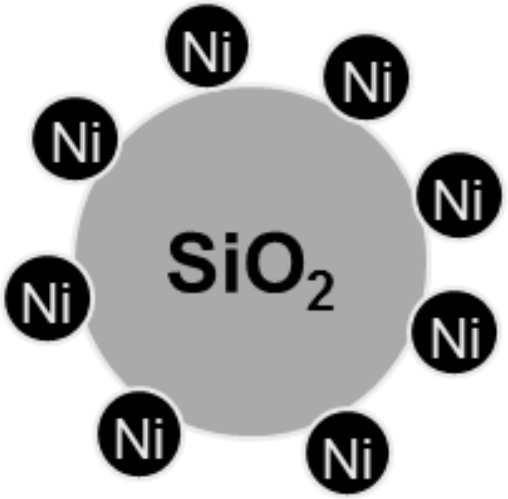

Ni2p Scan
Fresh
Reduced
Tested
SiO2 / 1Ni
Counts x 10-3
Binding Energy (eV)


Ni2p Scan
Fresh
Reduced
Tested
Ni@SiO2
Counts x 10-3
Binding Energy (eV)

C 1s Peak – Tested Catalysts



Conclusions



Coking dominates degradation

Sintering dominates degradation

Future Work

- Long term testing
- Further characterisation
- Integration of the catalyst into a fuel cell

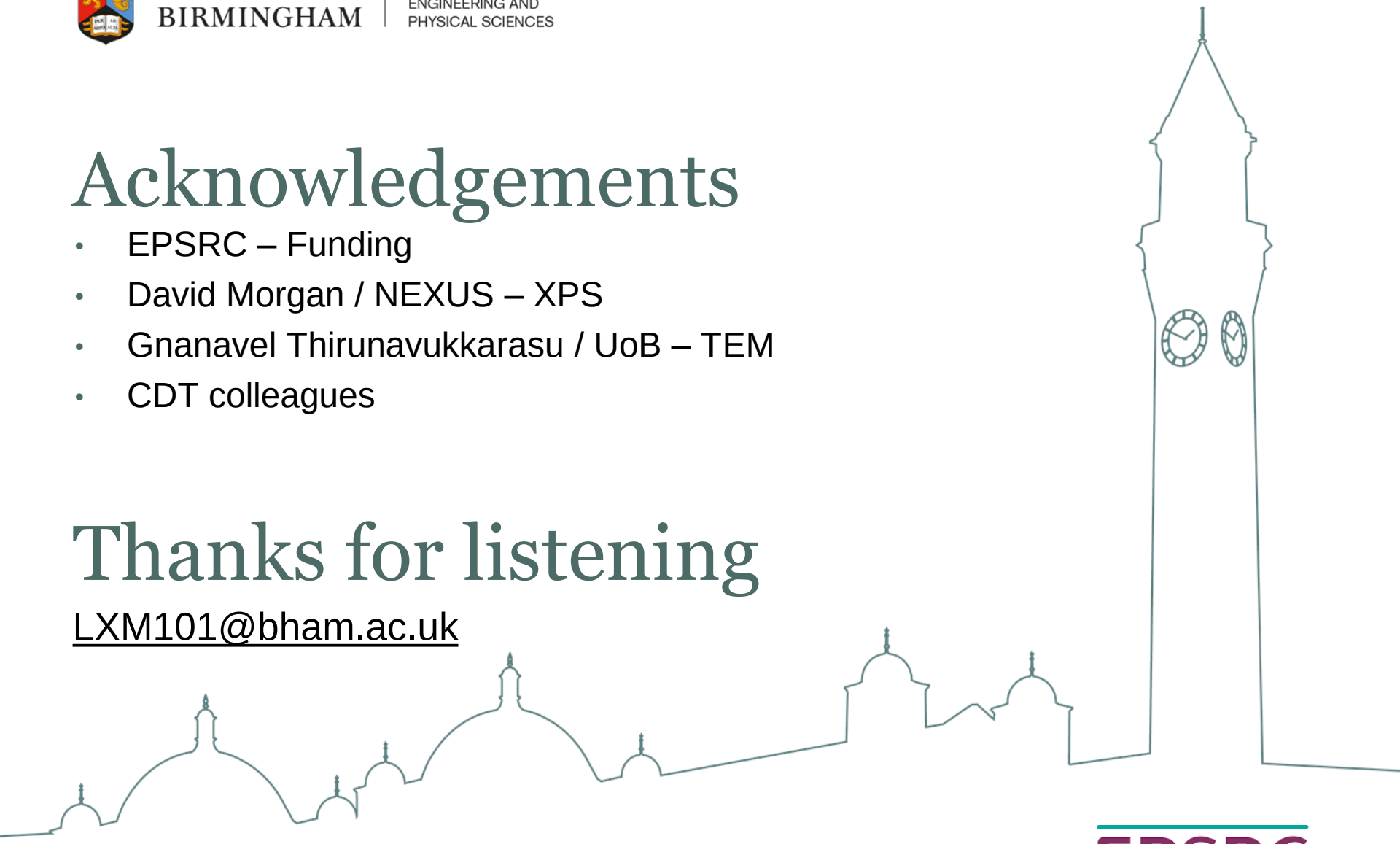
UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Acknowledgements

- EPSRC – Funding
- David Morgan / NEXUS – XPS
- Gnanavel Thirunavukkarasu / UoB – TEM
- CDT colleagues

Thanks for listening

LXM101@bham.ac.uk



EPSRC
Engineering and Physical Sciences Research Council