Autothermal oxidative decomposition of ammonia for hydrogen production

Student: Scott Bamforth, Supervisor: Peter Wells, Lindsay-Marie Armstrong (FEPS)

Introduction

The UK requires means to achieve a net zero carbon economy. Hydrogen is among the best candidates for solving this issue but has innate storage and transport difficulties in its natural state. Therefore, it requires liquid storage and transport vectors for use on a large scale, such as the shipping industry. Ammonia is currently one of the top contenders for this due to its high hydrogen content and existing routes of synthesis.

Ammonia can be cracked by applying heat to release the hydrogen where it is required. This can be done through the autothermal coupling of ammonia decomposition (+45.9 $kJmol^{-1}$) and oxidation (-317 $kJmol^{-1}$) which has been shown to provide enough heat to allow for external temperature and energy input requirements to be reduced [1]. Ruthenium-based catalysts have shown the greatest activity for this reaction.

Aims and Objectives

The aim of this project is to recreate the overlap between ammonia decomposition and oxidation at low temperature and to characterize the temperature of the nanoparticle surface across the catalyst bed. This is done by x-ray absorption spectroscopy and utilises the relationship between temperature and the mean squared disorder parameter (σ^2). Linear combination fitting can be used to determine the composition at different temperatures, which is done by characterising the magnitude of the oscillations produced in the EXAFS (Extended X-ray absorption fine structure).

This information can then be used to evaluate the efficiency of the paired reaction and methods can be considered to improve it, particularly in respect to reactor design and gas flow parameters. Additionally, bimetallic catalysts can be used to reduce the amount of ruthenium needed, as it is rare and expensive.

Results and Discussion

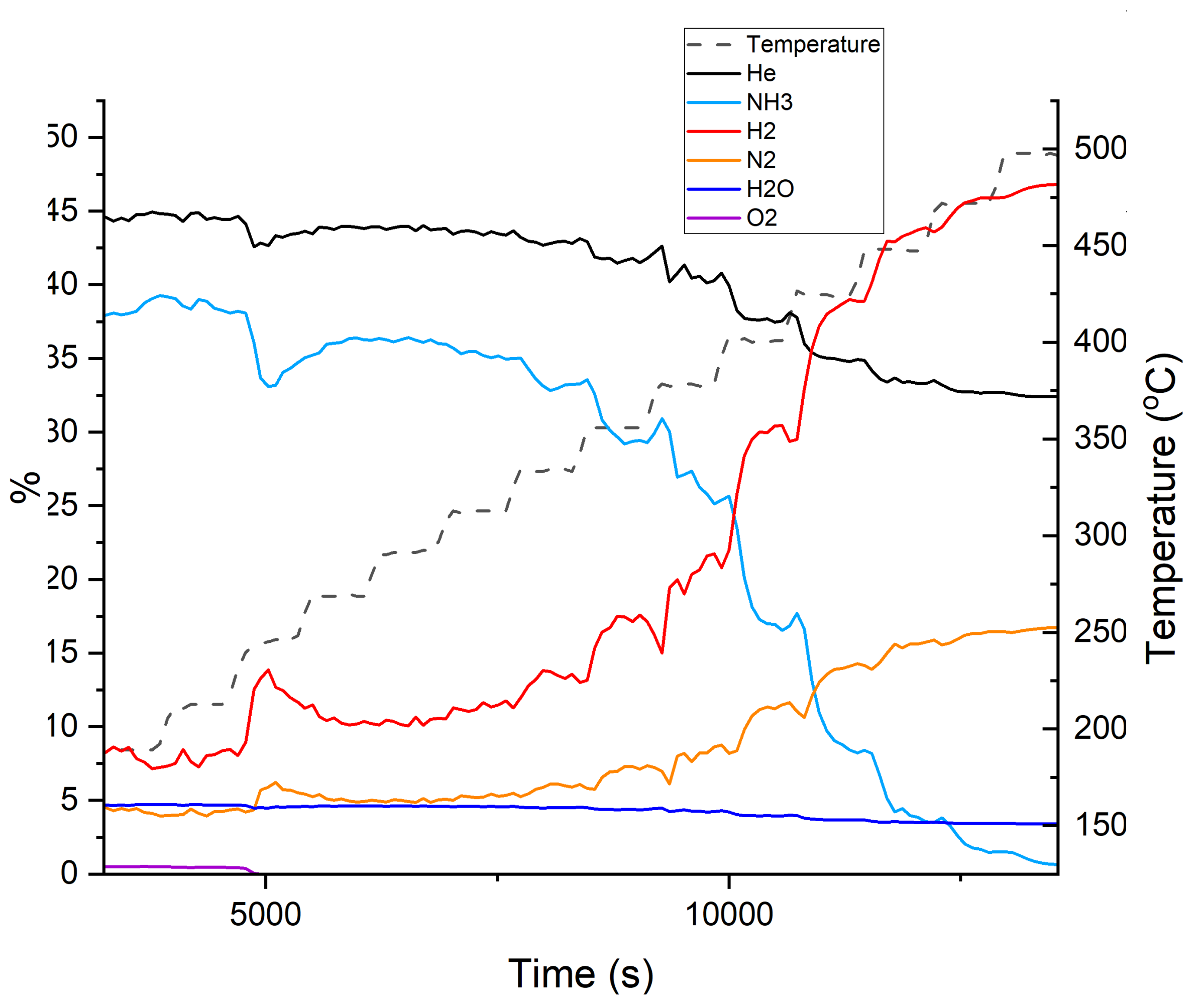


Fig. 1: Gas mix at outlet of reactor from mass spectrometry. 200mg 12-16nm RuO_2/Al_2O_3 (5%wt Ru), 100:25:13.87mL/min NH_3:O_2:He

(Left)

- Brief overlap of NH_3 oxidation and decomposition ~250°C
- Decomposition increase after 350°C
- ~Total conversion by 500°C
- Conversion near 0% by this stage without catalyst present
- At this stage the overlap is imperfect and needs to be re-visited with different conditions
- An additional co-feed of argon may be employed to prevent excessive water flooding the mass spectrometer

(Right)

- XANES (X-ray absorption near edge structure) of RuO_2 catalyst at 250°C, NH_3/O_2 flow
- Different structures observed between inlet and outlet ends of the catalyst bed
- Inlet matches ruthenium oxide, outlet matches ruthenium metal, mixed phase in the middle
- Models for the oxide, metal, and mixed phase to determine the disorder (and temperature) created in Artemis software (for EXAFS analysis) from calibrations
- Catalyst bed composition determined from linear combination fitting in Athena

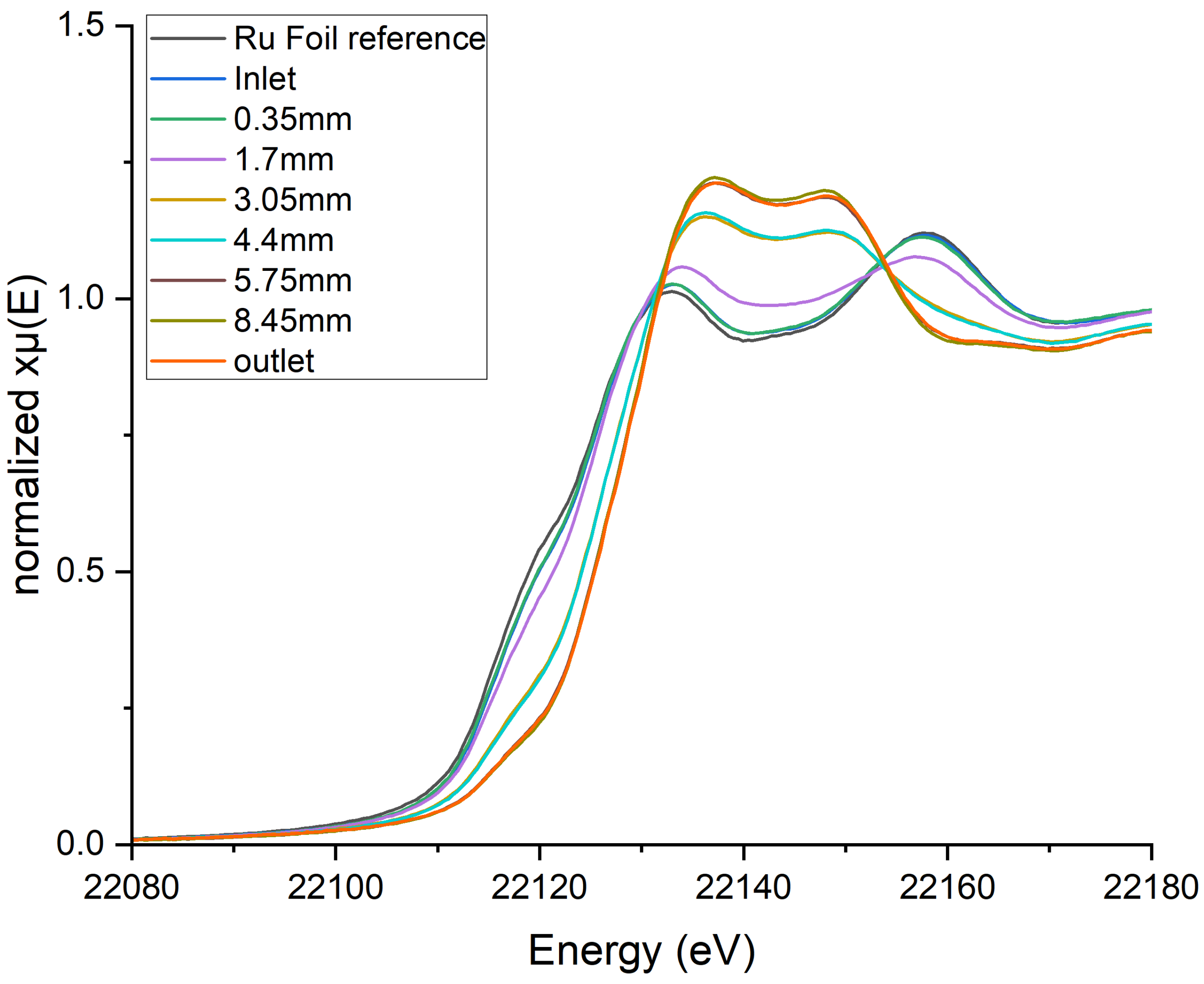
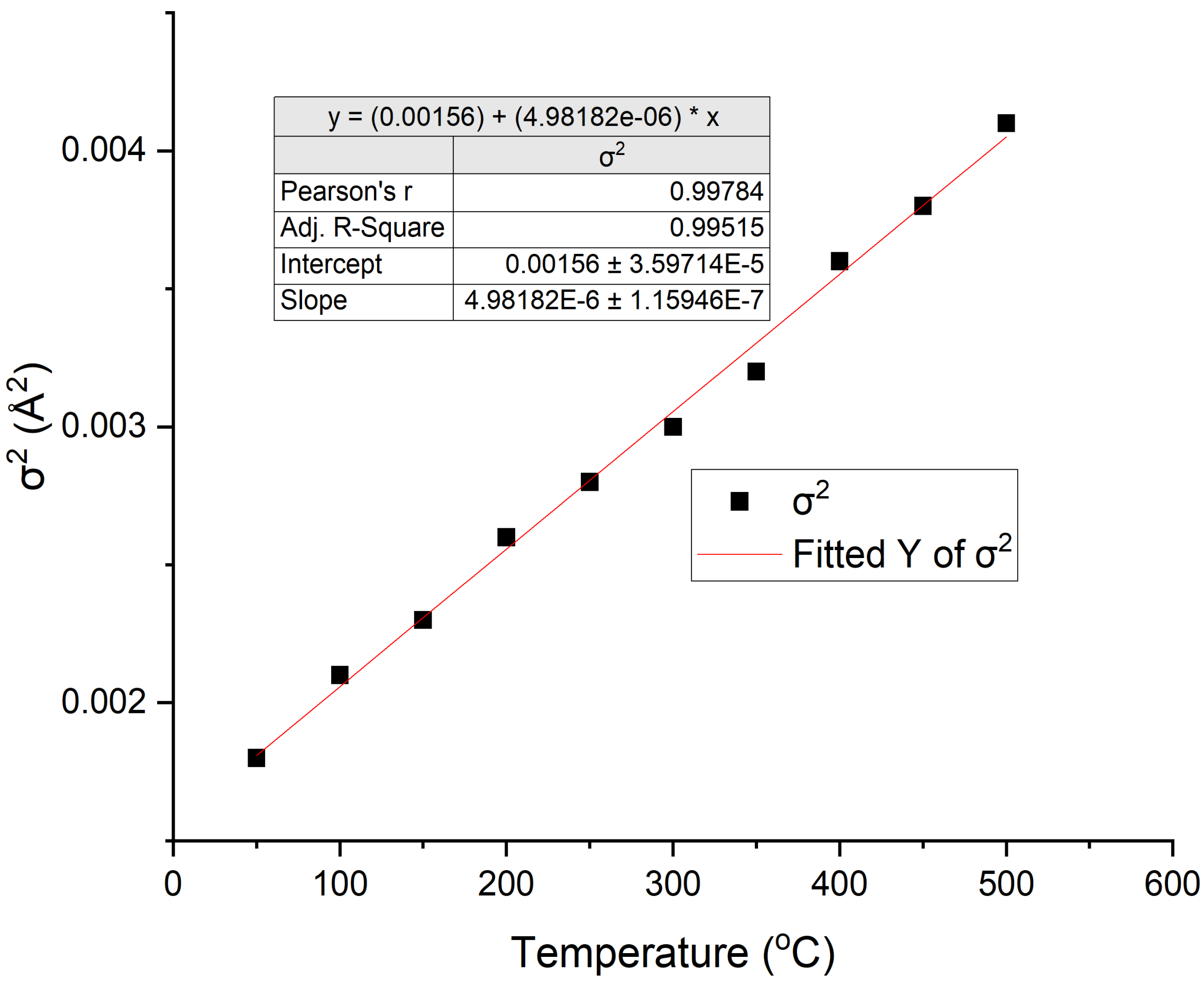


Fig. 2: XANES data across catalyst bed 40:10mL/min NH_3:O_2 flow. 50mg 5%wt RuO_2/Al_2O_3 (data taken at Diamond Light Source)



y = (0.00156) + (4.98182e-06) * x	
	σ^2
Pearson's r	0.99784
Adj. R-Square	0.99515
Intercept	0.00156 ± 3.59714E-5
Slope	4.98182E-6 ± 1.15946E-7

Fig 3. Thermal disorder parameter (Oxide) vs temperature calibration

- Mean squared thermal disorder parameters from Artemis model from ruthenium oxide calibration scans at known temperatures
- The equation generated from this was applied to scans taken under reaction conditions to find the temperature at the nanoparticle surface
- (This was applied to the oxidic and mixed phase part of the catalyst bed)
- Another calibration was carried out for metallic ruthenium

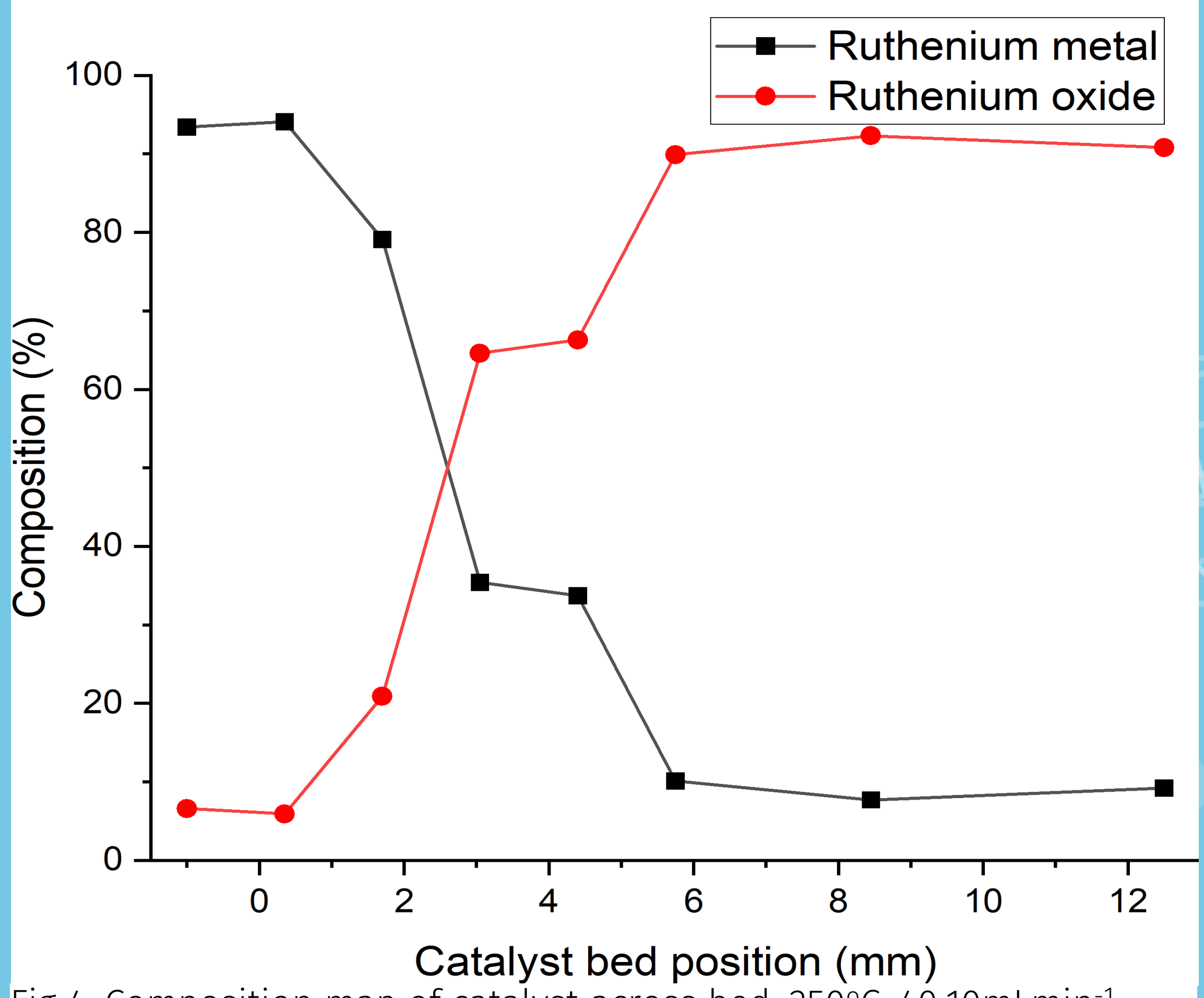


Fig 4. Composition map of catalyst across bed, 250°C, 40:10mLmin^{-1} NH_3:O_2

- Composition map of the catalyst bed determined from linear combination fitting in Athena software
- Used known standards of ruthenium oxide and ruthenium metal
- Indicates highly metallic catalyst towards the inlet and highly oxidic catalyst towards the outlet
- Small amount of metal present at the end of the bed, theorised at this stage to be small clusters amidst the oxide.
- Model initiated with pathways for RuO_2 from [2].

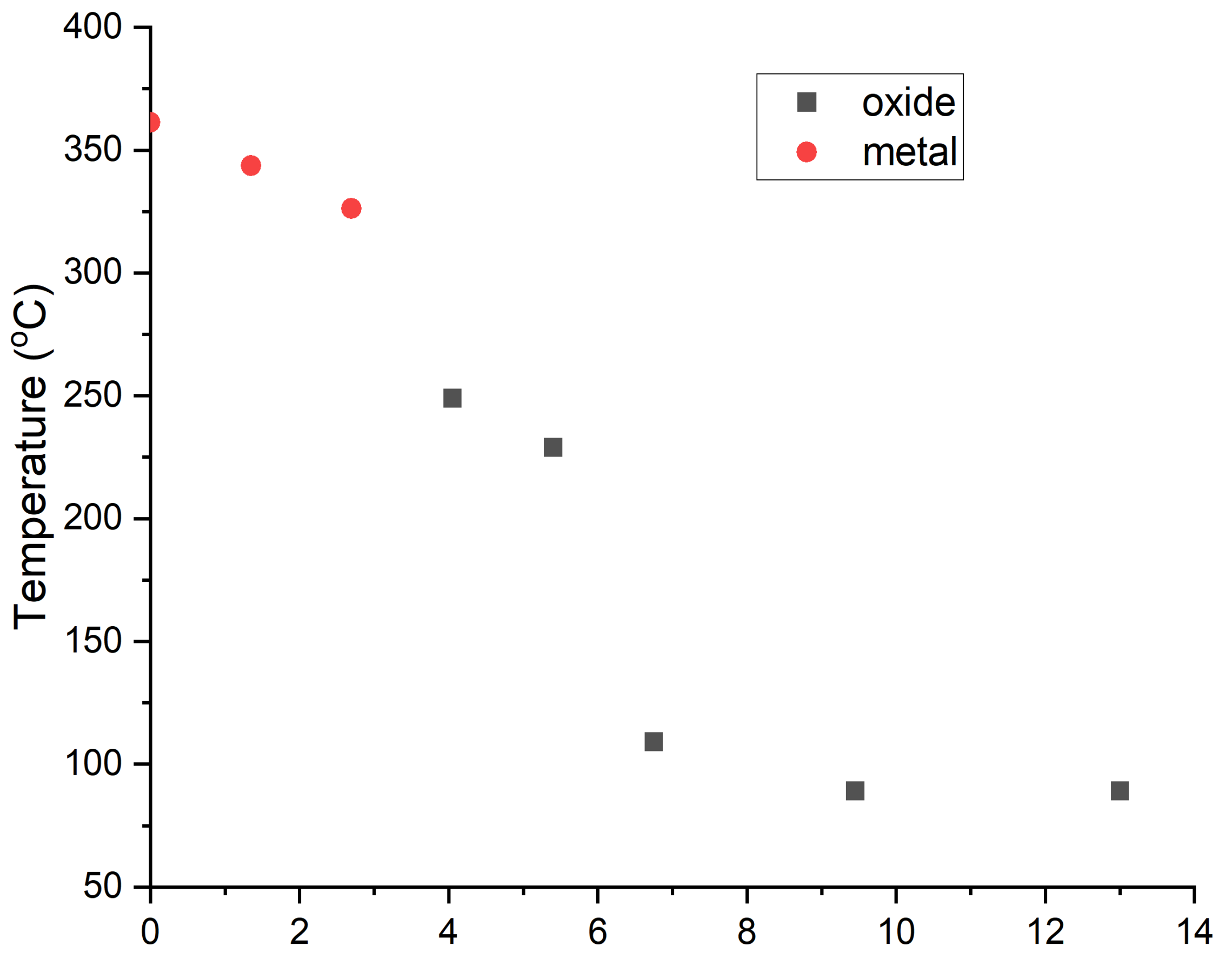


Fig 5. Temperature map of nanoparticle surface across catalyst bed, 250°C, 40:10 mLmin^{-1} NH_3:O_2

- Temperature map of catalyst bed determined from mean squared disorder parameters for Ru metal and Ru oxide using the mixed-phase Artemis model using method from [3]
- High temperature towards inlet indicates ammonia oxidation is likely to be occurring.
- Lower than expected temperature towards outlet indicates ammonia decomposition is likely to be occurring.
- Disorder parameters other than thermal may influence σ^2 values in mixed phase regions.

Further Work

Future work will involve running validation experiments for the XAS data with mass spectrometry to monitor the reactions, experiments to improve the overlap of ammonia oxidation and decomposition by altering reaction conditions and catalyst parameters, further XAS experiments to determine the mechanism behind the autothermal reaction, and investigations into improving the overall efficiency. The latter point may involve running fluid dynamics simulations to find suitable potential reactor designs.

Acknowledgement(s)

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References

[1] Nagaoka, K *et al*, 2017, Carbon-free H_2 Production from Ammonia Triggered at Room Temperature with an Acidic RuO_2/γ-Al_2O_3 Catalyst, Sci Adv, vol. 3, no. 4

[2] Mckeown, D *et al*, Structure of Hydrous Ruthenium Oxides: Implications for Charge Storage, 1999 The Journal of Physical Chemistry

[3] Gibson, E *et al*, Probing the Role of a Non-Thermal Plasma (NTP) in the Hybrid NTP Catalytic Oxidation of Methane, 2017, Angew Chem Int Ed Engl.