Ammonia as hydrogen carrier and carbon-free fuel

Dr Siqi Wang

Research Fellow in Chemical Engineering
Faculty of Engineering and Applied Sciences
Cranfield University

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Role of ammonia in a net-zero hydrogen economy

HyDEX

The limitations of hydrogen

- Challenges in hydrogen storage and transportation
- Production and sourcing of hydrogen
- Safety concerns due to high flammability

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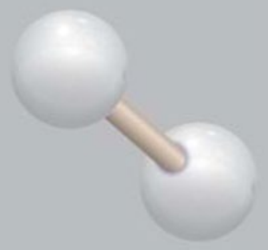
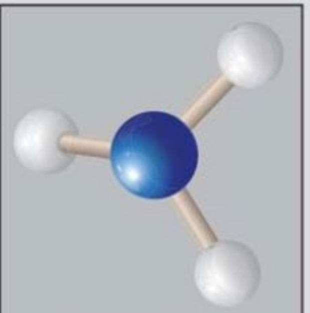
Role of ammonia in a net-zero hydrogen economy

Ammonia to the rescue?

- **Carbon-free hydrogen carrier** with a high hydrogen content of 18 wt.%.
- Higher volumetric energy density, smaller flammability range, easier leak detection due to distinctive smell.
- **Ease of storage and transportation**: liquid hydrogen (pressure ~700 bar, or below -253 °C) vs. liquid ammonia (~10 bar or lower when below -33 °C).
- **Established production method** (Haber-Bosch process) and can be adapted to use green hydrogen.
- **Existing infrastructure** and global networks for ammonia production, distribution, and storage.

	 HYDROGEN, H_2	 AMMONIA, NH_3
Volumetric energy density (MJ/L)	$10_{(l)}$, $6_{(g,\ 700\ bar)}$	$14_{(l)}$
Gravimetric energy density (MJ/kg)	142	23
Flammability limit (Equivalence ratio)	0.10–7.1	0.63–1.40
*Flammability hazard**	4	1
*Health hazard**	0	3

https://www.thechemicalengineer.com/features/h2-and-nh3-the-perfect-marriage-in-a-carbon-free-society/

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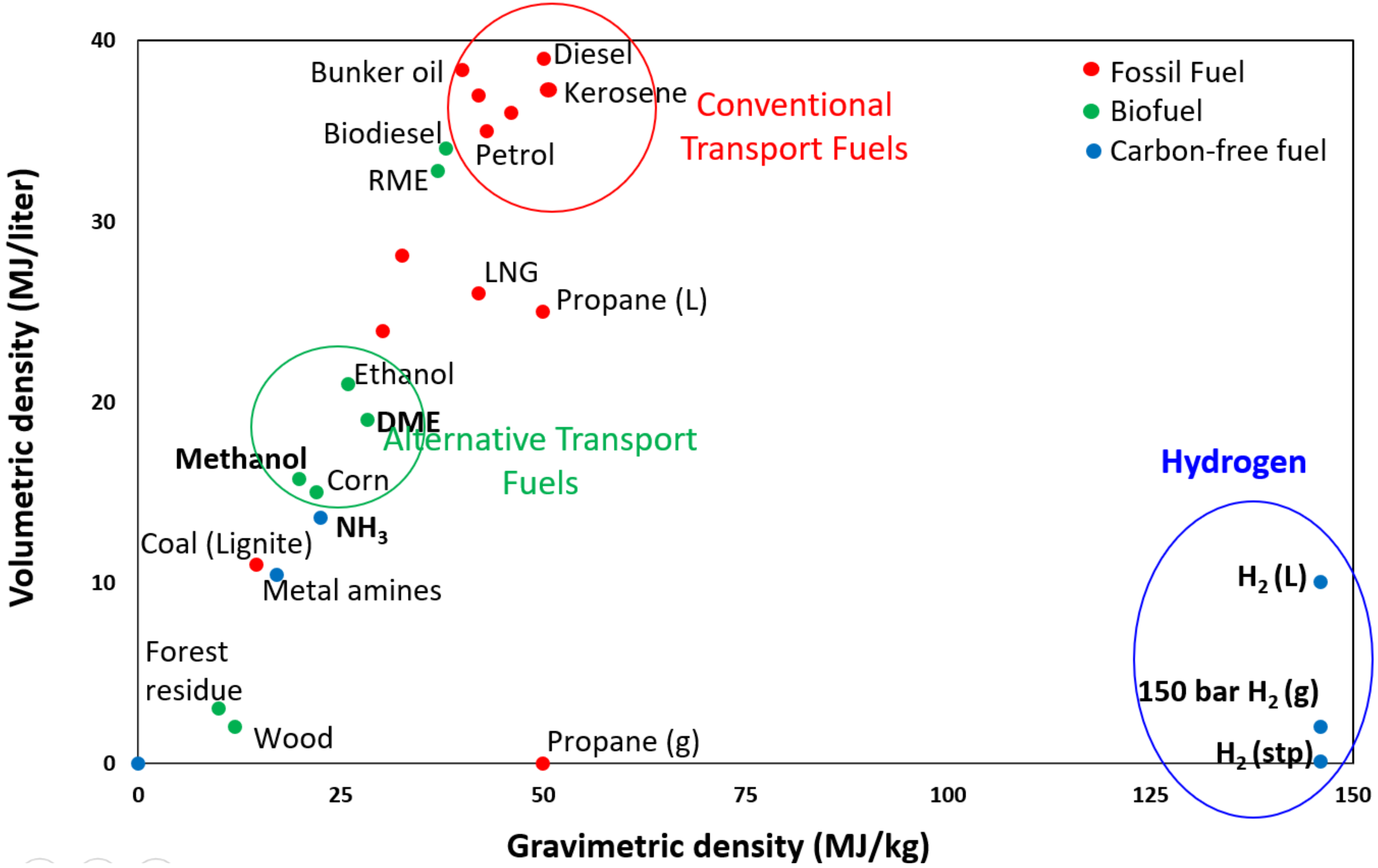
Energy density matters!



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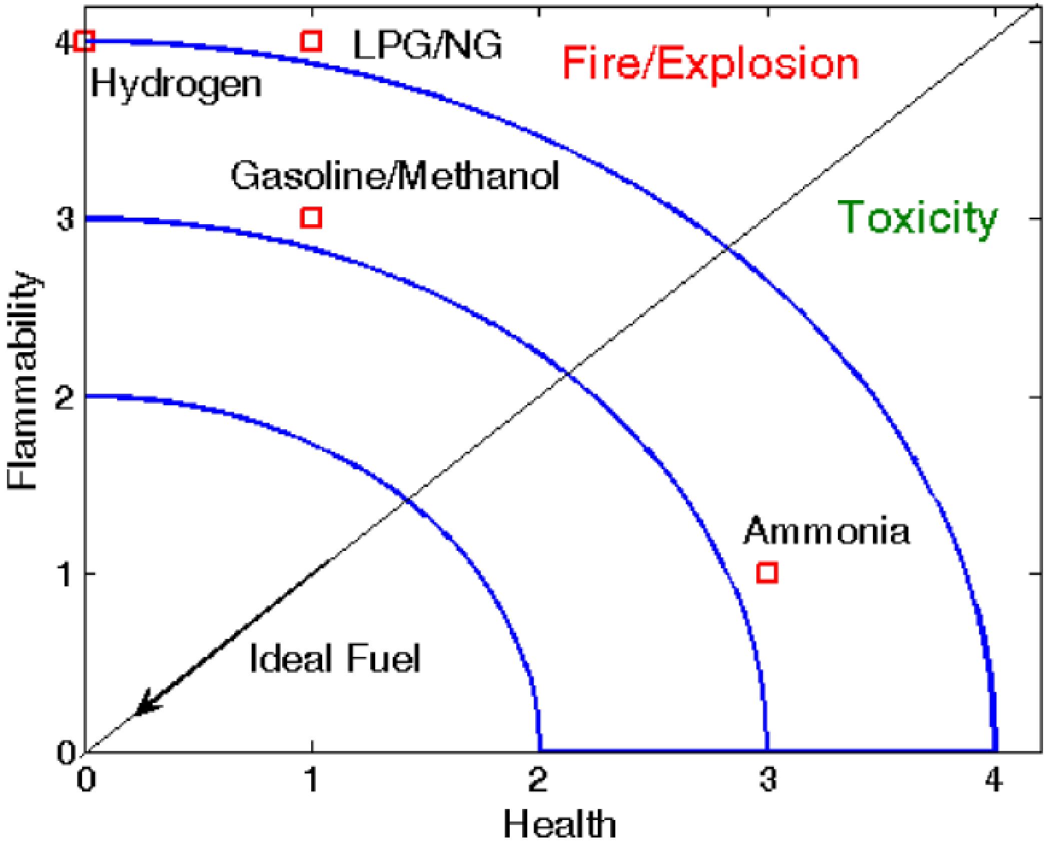
Safety concerns



- Ammonia vapor has a sharp pungent odour that acts as a warning for potentially dangerous exposure. The average odour threshold is 5 ppm, which is well below any danger or damage (50ppm over 8 hours).

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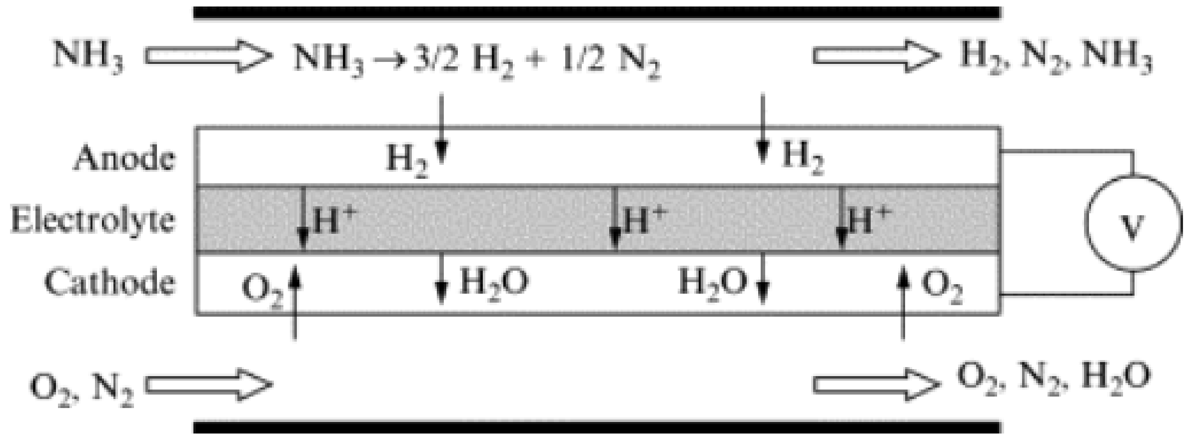
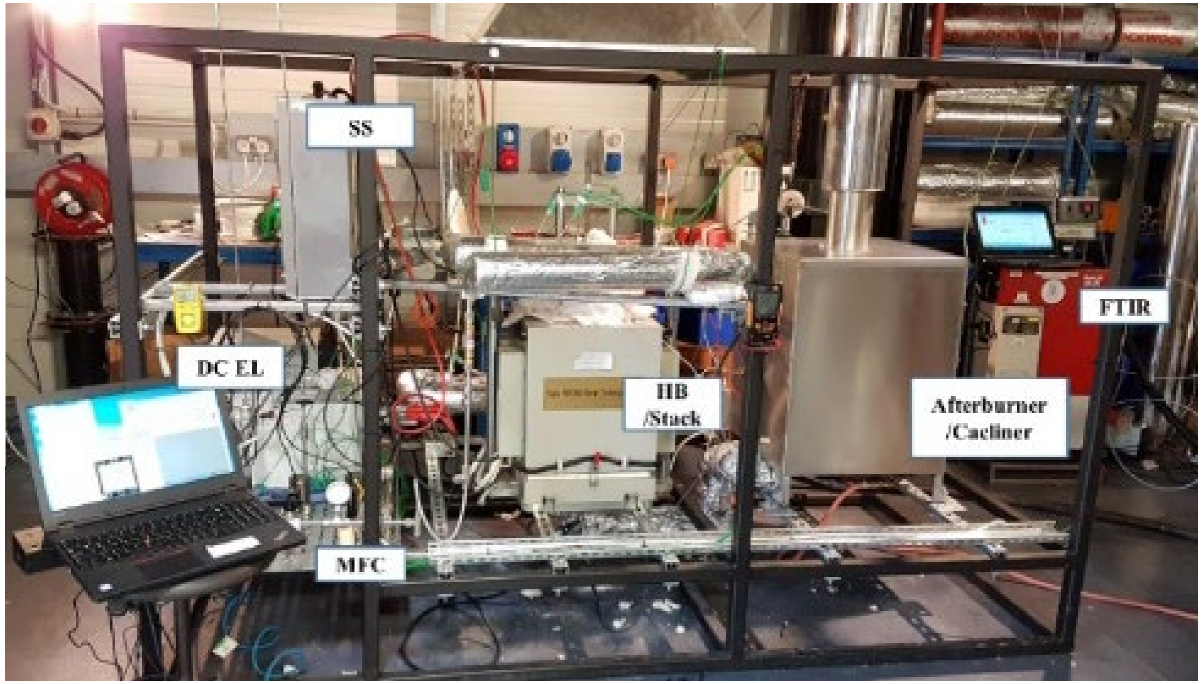
Overview of ammonia-related work at Cranfield University

- Ammonia solid oxide fuel cell
- Electrochemical ammonia cracking
- Catalytic ammonia decomposition
- Catalytic ammonia combustion
- …

Ammonia solid oxide fuel cell (SOFC)



- Same configuration of H_2 SOFC
- Direct power generation without NOx
- Handle low concentration of ammonia
- Challenges are the catalyst stability



5 kW SOFC system at Cranfield

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Electrochemical ammonia cracking

General Description

Anode: $2NH_3 + 6OH^- \longrightarrow N_2 + 6H_2O + 6e^-$

$E(vs\ SHE) = -0.77\ V$

Cathode : $6H_2O + 6e^- \longrightarrow 3H_2 + 6OH^-$

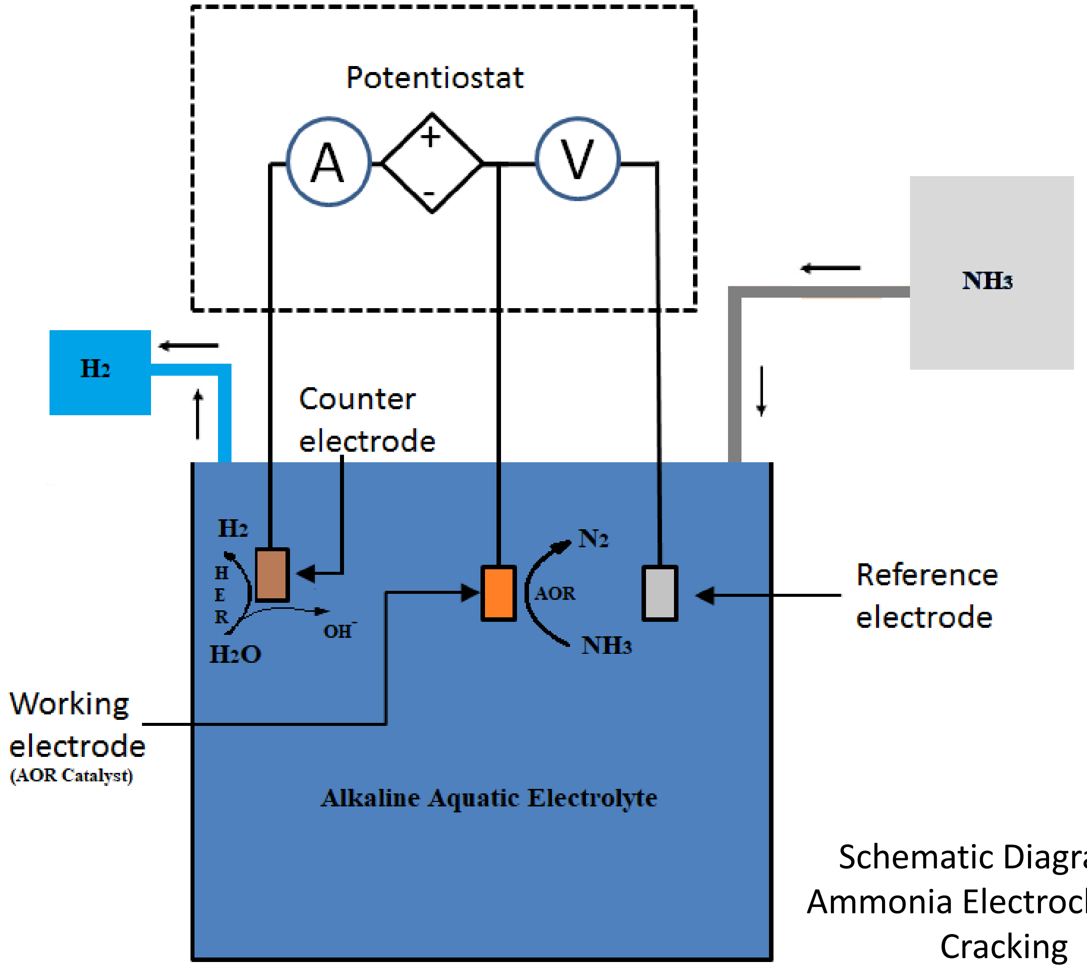
$E(vs\ SHE) = -0.83\ V$

Total : $2NH_3 \longrightarrow N_2 + 3H_2$

$E = 0.06\ V$

$E_{H_2O} = 1.23V$

- Theoretical energy consumption is 95% lower than water electrolysis
  - AOR: $1.55 wh/gH_2$
  - HER: $33 wh/gH_2$



Schematic Diagram of Ammonia Electrochemical Cracking

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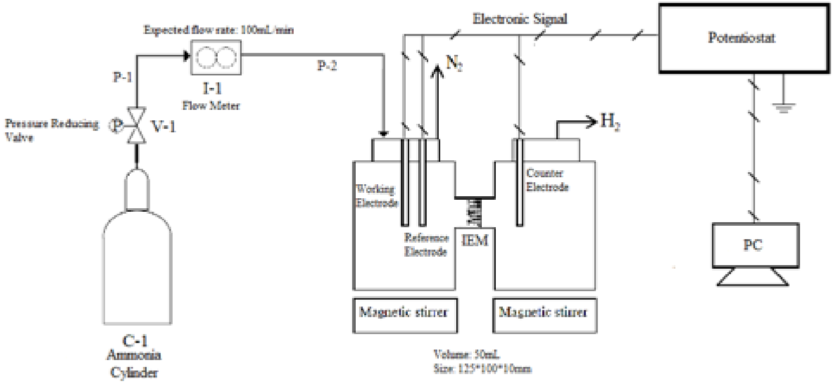
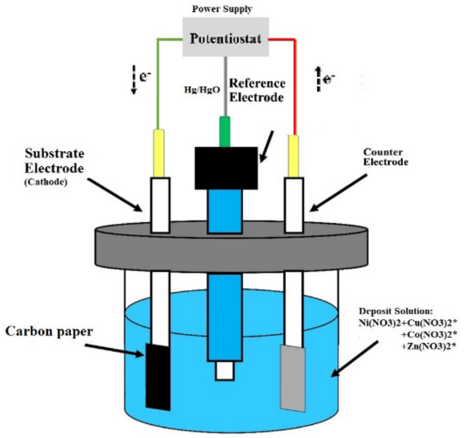
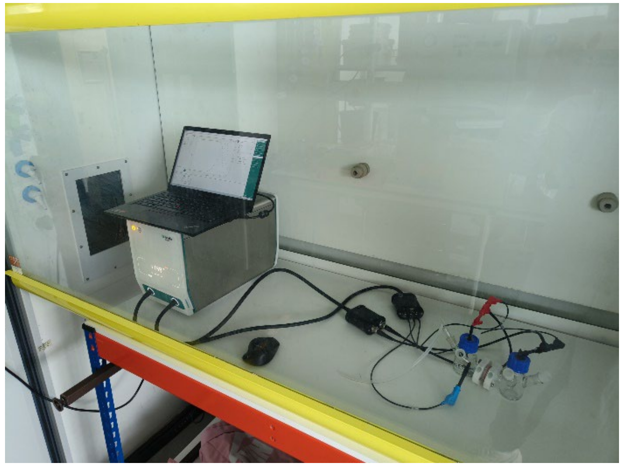
Electrochemical ammonia cracking

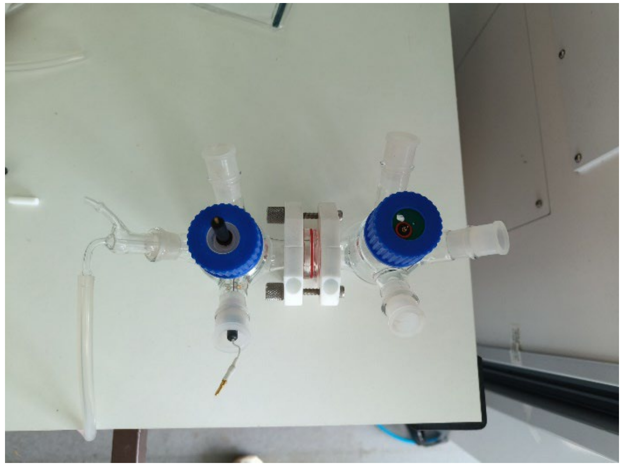


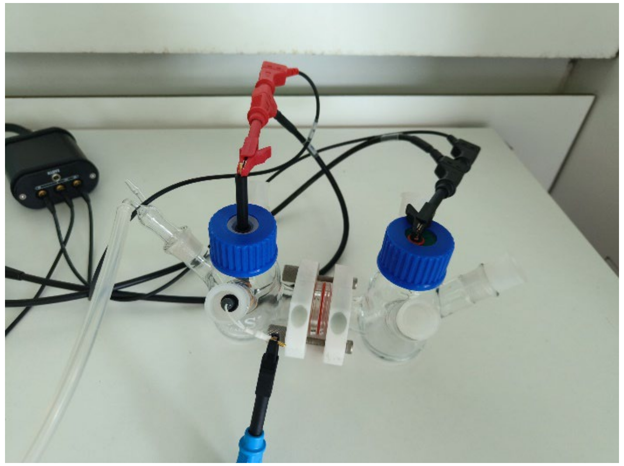
Schematic Diagram of Electrochemical Reactor



Schematic Diagram of Electrodeposition Reactor







Project funded by EDF

Ammonia source options:

- First phase: 0.1M $NH_3 \cdot H_2O$
  (For rapid screening samples)
- Second phase: Ammonia gas pipeline system
  (For more detailed testing of samples' electrochemical performance)

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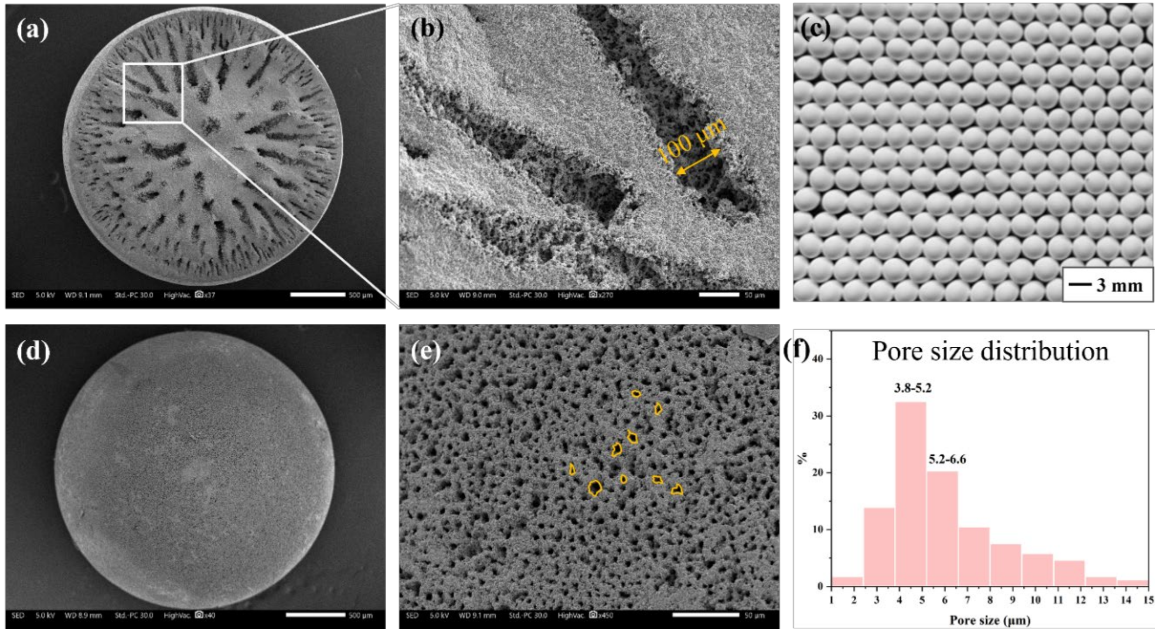
Catalytic ammonia decomposition for hydrogen production

Highly porous alumina with structured microchannels



SEM images of (a, b) the cross-sectional view
(d, e) the surface view of Al_2O_3-A
(f) the size distribution of open channels on the surface of Al_2O_3-A
(c) its whole view.

$$NH_3 + * \leftrightharpoons NH_3^* \quad (1)$$

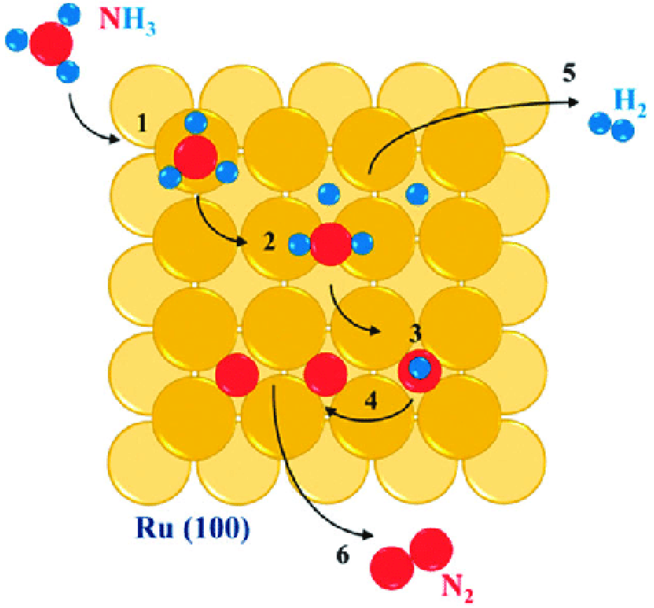
$$NH_3^* + * \leftrightharpoons NH_2^* + H^* \quad (2)$$

$$NH_2^* + * \leftrightharpoons NH^* + H^* \quad (3)$$

$$NH^* + * \leftrightharpoons N^* + H^* \quad (4)$$

$$H^* + H^* \leftrightharpoons H_2 + 2^* \quad (5)$$

$$N^* + N^* \leftrightharpoons N_2 + 2^* \quad (6)$$



Elementary reaction steps involved in the ammonia decomposition reaction on a noble metal-based catalyst.

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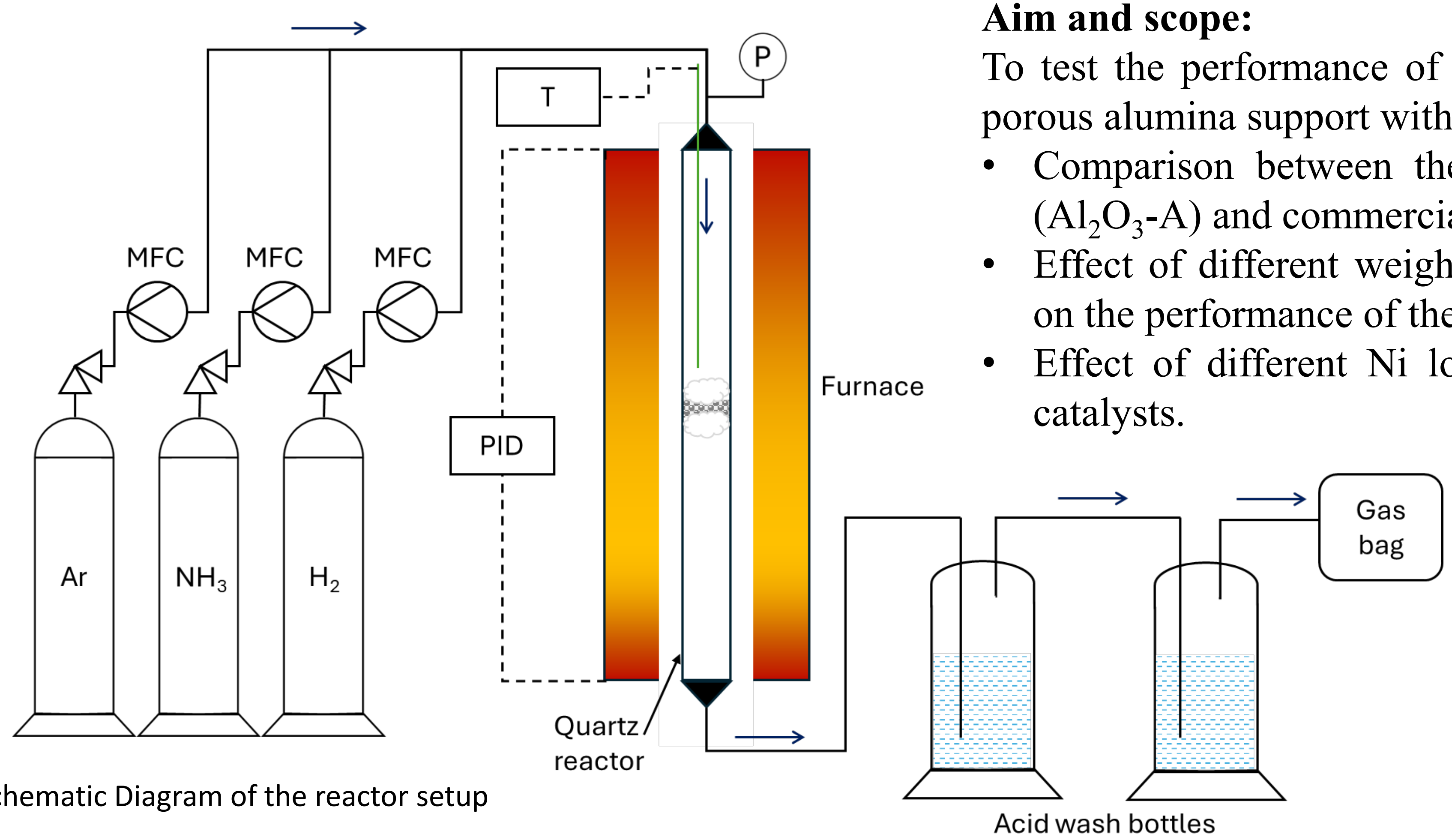
Catalytic ammonia decomposition for hydrogen production



Schematic Diagram of the reactor setup

Aim and scope:

To test the performance of Ni catalysts supported on a novel porous alumina support with structured microchannels.

- Comparison between the microchannel-structured support (Al_2O_3-A) and commercial alumina pellets (Al_2O_3-B).
- Effect of different weight hourly space velocities (WHSV) on the performance of the catalysts.
- Effect of different Ni loading on the performance of the catalysts.

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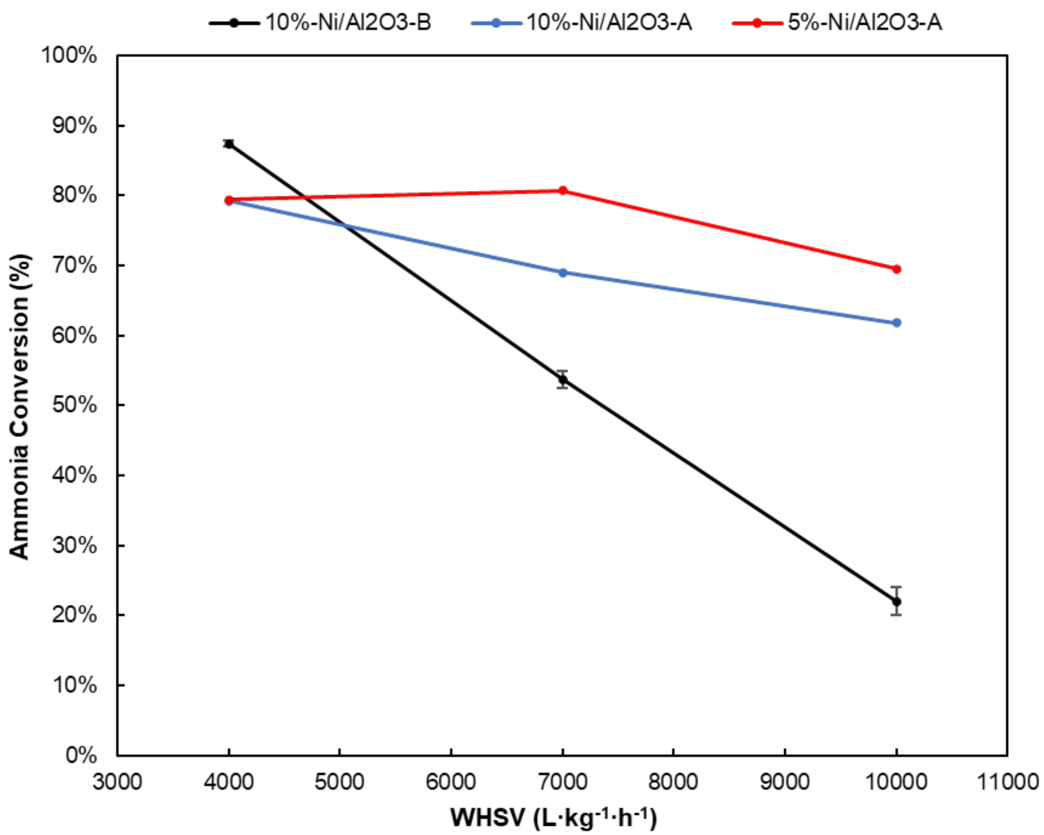
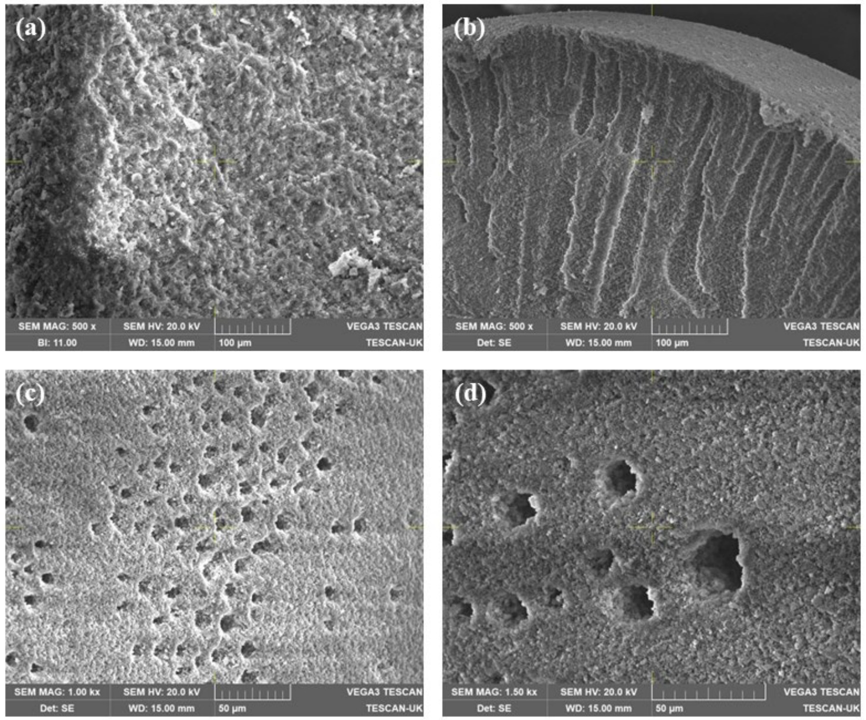
Catalytic ammonia decomposition for hydrogen production



Ammonia conversion achieved by the catalysts.



SEM images of (a) the commercial Al_2O_3-B support
(b) the cross-sectional view of the used 10-Al_2O_3-A
(c, d) the surface view of the used 5-Al_2O_3-A and 10-Al_2O_3-A.

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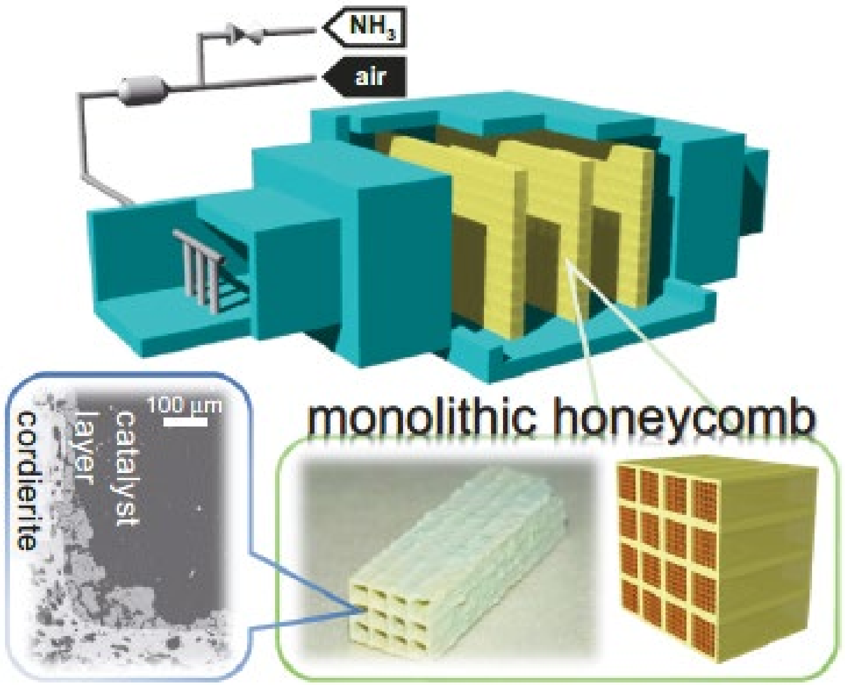
Catalytic ammonia combustion

- Pt- and Pd-based catalysts widely used for catalytic ammonia oxidation processes (e.g. treating low-concentration NH_3 as a pollutant, converting NH_3 to NO for nitric acid production)
- Existing research on ammonia combustion catalysts:
  - CuO-based catalysts supported on ceramic materials.
  - Noble metal-based catalysts, e.g. Pt/Al_2O_3.
  - Bimetallic catalysts, e.g. supported Cu-Ag, Cu-Ru catalysts.
  - Structured catalysts.

CuO-based catalysts with different support materials



Honeycomb $CuO-Al_2O_3$ catalyst. Ammonia Combustion Properties of Copper Oxides-based Honeycomb and Granular Catalysts (jst.go.jp)

Numerical simulations – DFT-based calculations

- **Density Functional Theory (DFT):**
  - A computational quantum mechanical modelling method used to investigate the electronic structure of atoms, molecules, and solids.
- **Application of DFT in catalysis:**
  - Interaction between catalysts and reactants at an atomic level.
  - Active sites identification.
  - Reaction pathway identification.
  - Widely applied in hydrogen-related studies for catalyst development [1,2]

[1] Wang S, Nabavi SA, Clough PT. A review on bi/polymetallic catalysts for steam methane reforming. Int J Hydrogen Energy 2023;48:15879–93. https://doi.org/10.1016/j.ijhydene.2023.01.034
[2] Wang S, Shen Z, Osatiashtiani A, Nabavi A, Clough P. Ni-Based Bimetallic Catalysts for Hydrogen Production Via (Sorption-Enhanced) Steam Methane Reforming. https://doi.org/10.1016/j.cej.2024.150170

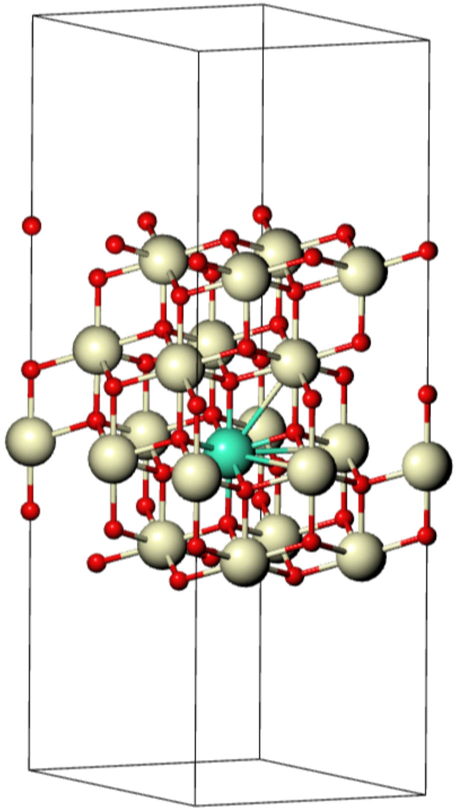
DFT-based calculations: Model construction

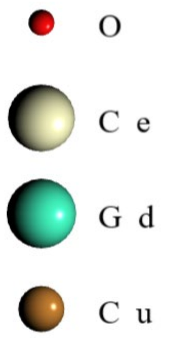
- Slab models are used to simulate the surface, bulk structure, and reaction environment of the catalysts under real-life conditions.

Top layers relaxed to simulate surface reconstruction

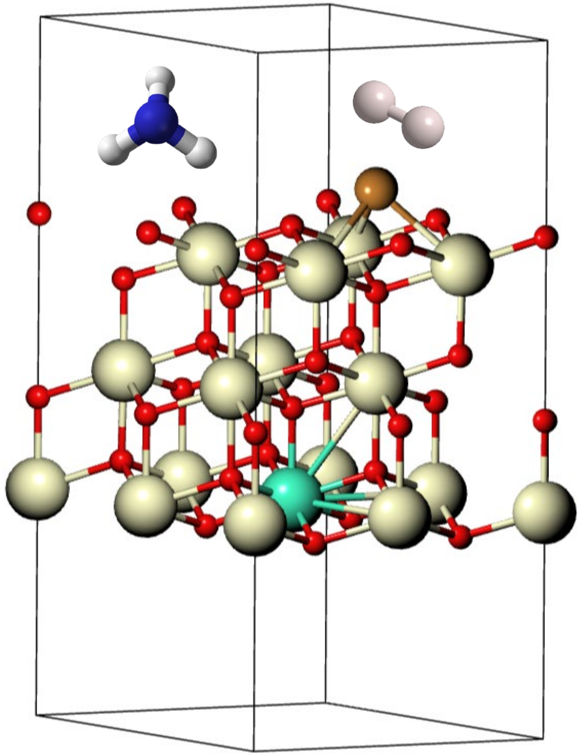
Bottom layers fixed to simulate bulk structure of the catalyst

GDC slab model





CuO-GDC slab model



Adding NH_3, H_2, and other molecules or atoms to study the adsorption and desorption energetics

Doping of Cu and Ge atoms to achieve the desired molar ratios

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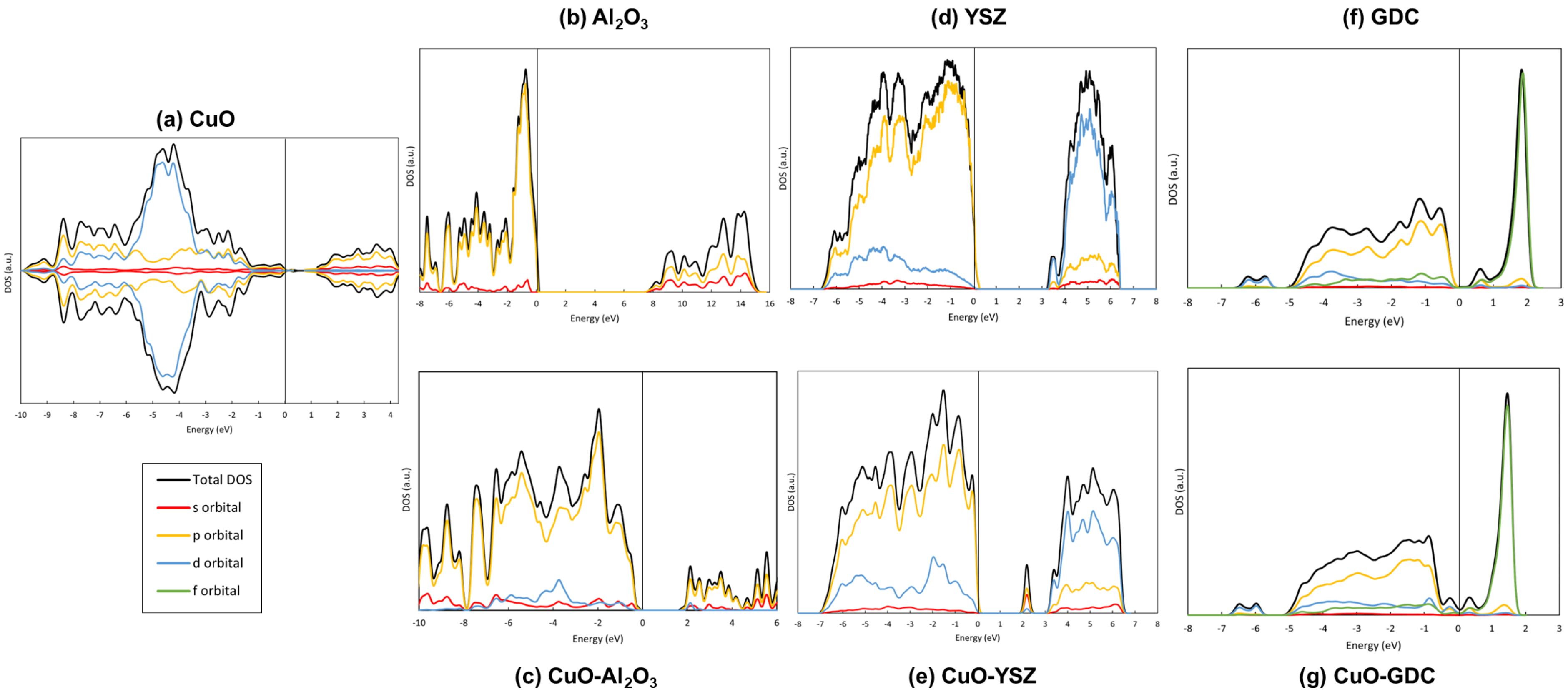
DFT-based calculations: Results



Density of states (DOS) plots of the bare supports and the supported catalysts.

- Smaller band gap → increased electronic conductivity.
- More states near the fermi level → better electron transfer between the catalyst and the reactants, which can enhance catalytic activity.

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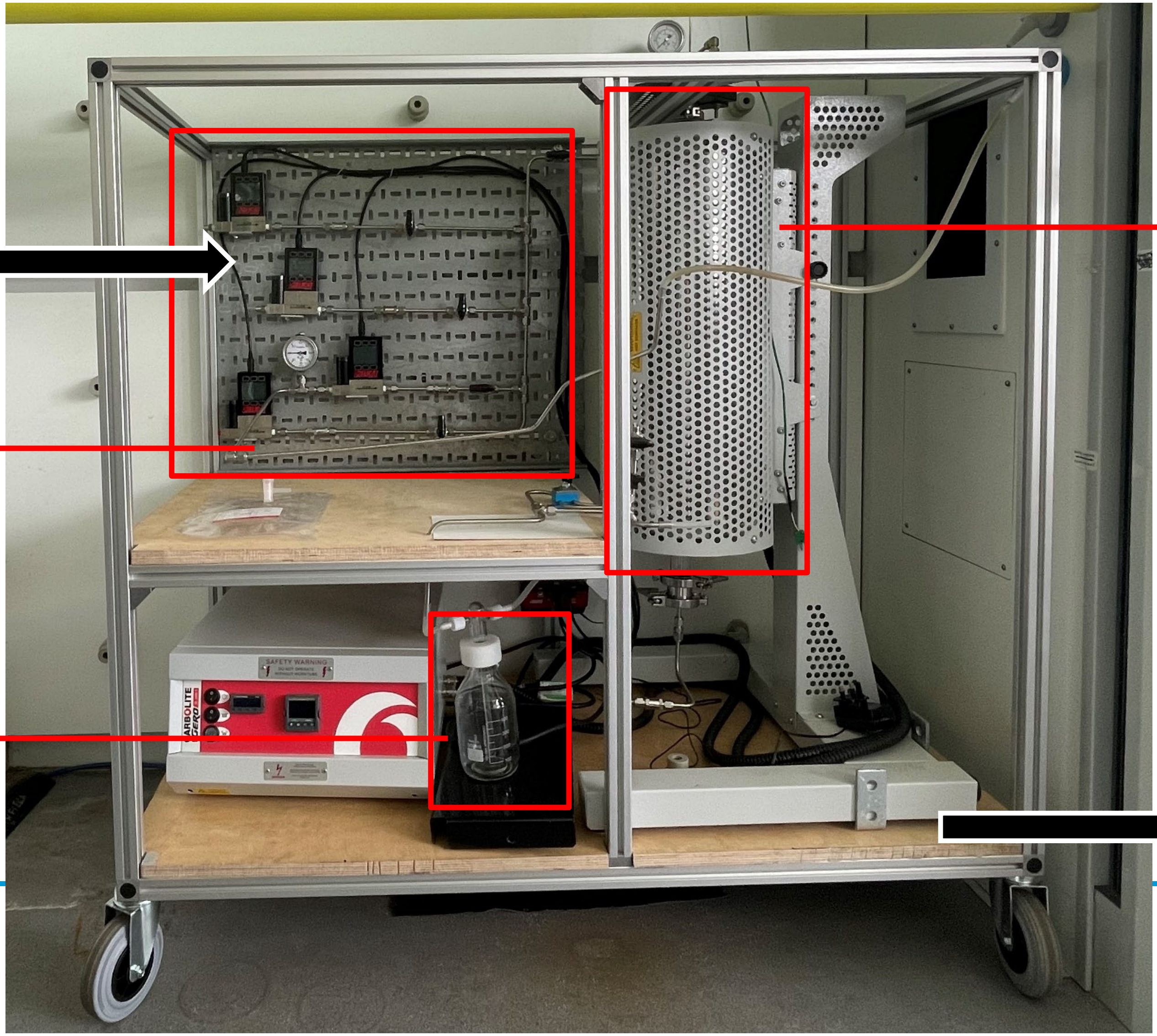
Experimental design and setup

Inlet gas composition: NH_3, O_2, and Ar

Mass flow controllers for inlet gas flow rate regulation

Acid trap for ammonia measurement



Tube furnace and quartz reactor

Outlet gas composition measured by GC-TCD and gas analysers

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Acknowledgment

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- Stopford
- MicroTech

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Thank you for your attention.

Dr Siqi Wang
Research Fellow in Chemical Engineering
Faculty of Engineering and Applied Sciences
Cranfield University
E: siqi.wang2019@cranfield.ac.uk
LinkedIn: https://www.linkedin.com/in/siqi-wang-a5ab6a1b5/
Twitter/X: @siqiwang55

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