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Development of an *operando* microreactor for combined X-ray absorption and vibrational spectroscopy to investigate the Reverse Water Gas Shift reaction.

Ruby Morris, University of Glasgow

02/12/2024



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Outline

1. Importance of CO₂ utilisation
2. The reverse water gas shift (RWGS) reaction
3. Oxygen storage capacity measurements – an insight into improving the catalytic activity of the RWGS.
4. Operando studies – Complementary spectroscopic techniques
5. Microreactors as a tool for improved catalytic design.



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CO₂ utilisation for a 'circular economy'

- Following COP26 in Glasgow, parties pledged to strengthen their climate action policies in order to limit the increase in global average temperature increase to 1.5 degrees.¹

- CO₂ utilisation offers an alternative to the current economic model and drives the shift towards a 'circular economy' in which CO₂ is recycled, and emissions are significantly reduced.

- **Carbon utilisation** = Technologies based on the transformation of CO₂ into a high-value feedstock.

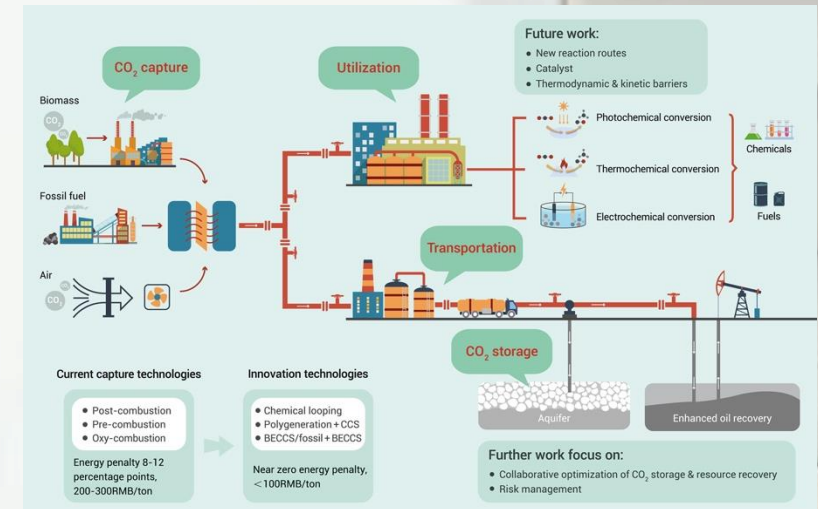


Figure 1. Roadmap for the implementation of CO₂ capture technology in industry.²

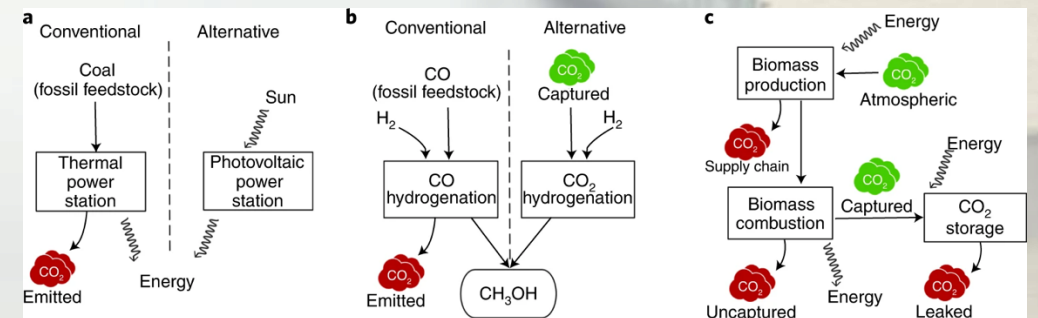


Figure 2. Emissions mitigation options.³

1. M. González-Castaño, B. Dorneanu and H. Arellano-García, The reverse water gas shift reaction: a process systems engineering perspective, *React Chem Eng*, 2021, 6, 954–976.

2. Raza, S., Ghasali, E., Raza, M., Chen, C., Li, B., Orooji, Y., Lin, H., Karaman, C., Karimi Maleh, H., & Erk, N. (2023). Advances in technology and utilization of natural resources for achieving carbon neutrality and a sustainable solution to neutral environment. *Environmental Research*, 220, 115135.

3. Babacan, O., De Causmaecker, S., Gambhir, A. *et al.* Assessing the feasibility of carbon dioxide mitigation options in terms of energy usage. *Nat Energy* 5, 720–728 (2020).
<https://doi.org/10.1038/s41560-020-0646-1>



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- The **RWGS** has been broadly investigated as reaction which may be implemented into carbon utilization technologies.
- **RWGS** = the reduction of CO₂ to CO.



- CO, a major component of syngas, can be easily obtained and further utilized in the manufacturing of other vital industrial chemicals including methanol and Gasoline.⁴
- Syngas conventionally derived from Fossil fuels.
- The RWGS offers a ‘decarbonized’ feedstock source.

The RWGS in industry – transforming CO₂ into high-value feedstocks

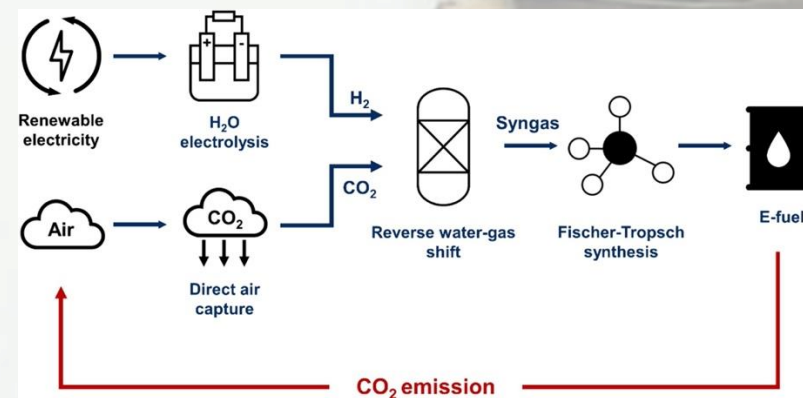


Figure 3. Schematic of the production of fuel via the RWGS.⁴

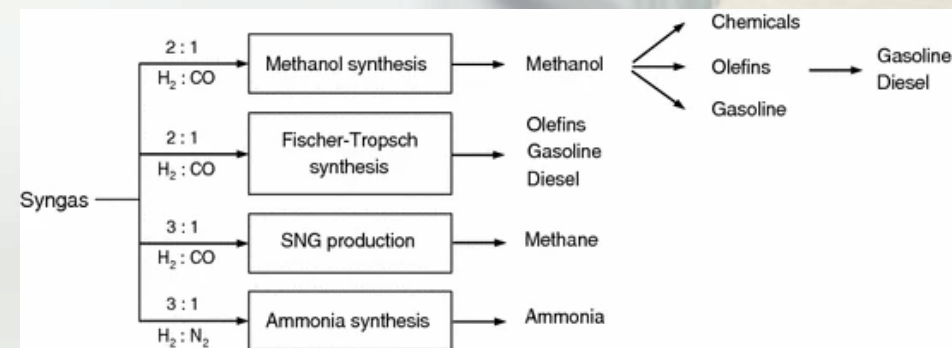


Figure 4. Syngas utilisation routes.⁵

4. Choi, Y., Sim, G. D., Jung, U., Park, Y., Youn, M. H., Chun, D. H., Rhim, G. B., Kim, K. Y., & Koo, K. Y. (2024). Copper catalysts for CO₂ hydrogenation to CO through reverse water–gas shift reaction for e-fuel production: Fundamentals, recent advances, and prospects. *Chemical Engineering Journal*, 492, 152283.

5. Litvinenko, V., Meyer, B. (2018). Syngas Utilization Technologies. In: Syngas Production: Status and Potential for Implementation in Russian Industry. Springer, Cham.



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- CO_2 has a high thermodynamic stability
- Forward reaction is moderately endothermic, elevated temperatures are thermodynamically favoured.⁴
- High temperatures favoured by the thermodynamic equilibrium are costly and energy-intensive.
- Numerous studies are being undertaken to optimise the RWGS reaction parameters and to improve CO_2 conversion and CO selectivity.

The reverse water gas shift (RWGS) – kinetic and thermodynamic barriers

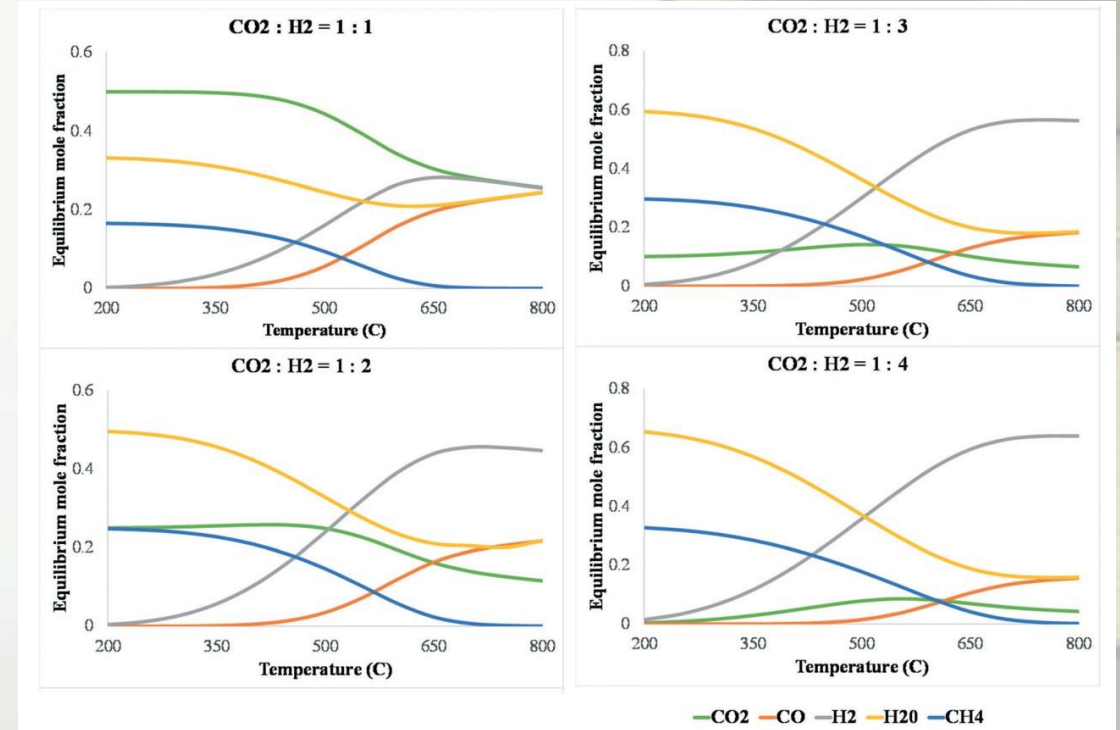


Figure 5. Influence of temperature on the equilibrium of the RWGS reaction (at 1 bar).⁶

6. González-Castaño, M., Dorneanu, B., & Arellano-García, H. (2021). The reverse water gas shift reaction: a process systems engineering perspective. *Reaction Chemistry & Engineering*, 6(6), 954–976. 4. Yamaoka, M., Tomozawa, K., Sumiyoshi, K. *et al.* Efficient reverse water gas shift reaction at low temperatures over an iron supported catalyst under an electric field. *Sci Rep* 14, 10216 (2024).



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Established catalysts - RWGS



Figure 6. Schematic of CeO₂ supported catalysts.⁷

| Catalyst | Temperature | Conversion | Selectivity |
|------------------------------------|-------------|------------|-------------|
| Cu/CeO ₂ ⁸ | 600 | 50 | 100 |
| 2%Pt-CeO ₂ ⁸ | 290 | 27.1 | 100 |
| Ni/ZrO ₂ ⁸ | 500 | 27.6 | 100 |

- Catalysts for industry applications must have high conversion and good selectivity at low temperatures to minimise cost and energy-use.
- Precious metals (Pt, Pd, Au, Ir, Rh) supported on oxides exhibit good activity however their commercial feasibility is limited by cost.
- Extensive interest in non-precious metals on reducible oxides catalysts, e.g. Cu/CeO₂.

7. Yan, H., Zhang, N., & Wang, D. (2022). Highly efficient CeO₂-supported noble-metal catalysts: From single atoms to nanoclusters. *Chem Catalysis*, 2(7), 1594–1623.

<https://doi.org/https://doi.org/10.1016/j.checat.2022.05.001>

8. Ebrahimi, P., Kumar, A., & Khraisheh, M. (2022). A Review of CeO₂ Supported Catalysts for CO₂ Reduction to CO through the Reverse Water Gas Shift Reaction. In *Catalysts* (Vol. 12, Issue 10). MDPI. <https://doi.org/10.3390/catal12101101>



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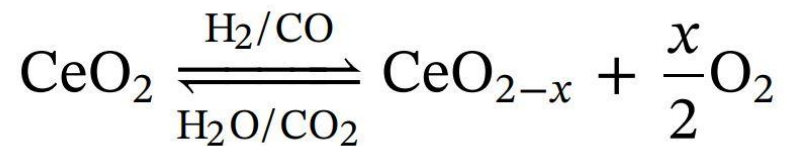


Figure 7. Reversible oxygen storage-release reaction of CeO_2 .⁹

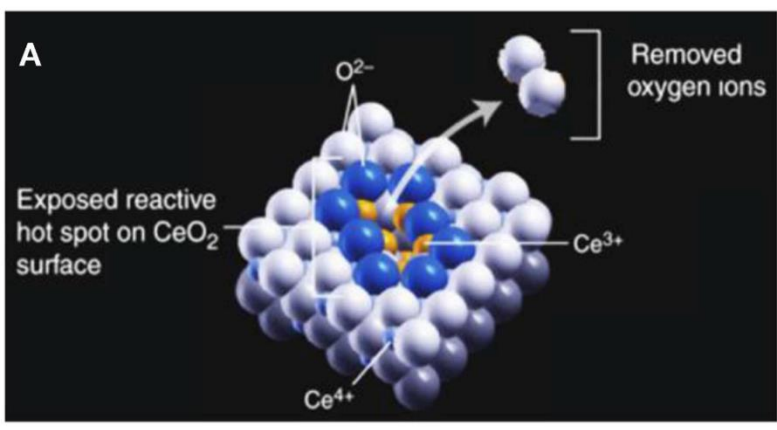


Figure 8. Illustration of the formation of a vacancy on the surface of ceria.⁹

9. S. Y. Ahn, W. J. Jang, J. O. Shim, B. H. Jeon and H. S. Roh, CeO_2 -based oxygen storage capacity materials in environmental and energy catalysis for carbon neutrality: extended application and key catalytic properties, *Catal Rev Sci Eng*, , DOI:10.1080/01614940.2022.2162677

Reducible oxides as catalytic supports

- High activity is thanks to the facile redox behaviour of cerium oxide (depending on feed in reactor stream).
- Transition between Ce^{4+} and Ce^{3+} allows for reversible oxygen storage and release.
- Ce^{4+} under oxidising conditions
- Ce^{3+} under lean conditions.
- Oxygen storage capacity describes the amount of reactive oxygen originating from the surface oxygen/oxygen vacancies of a material.

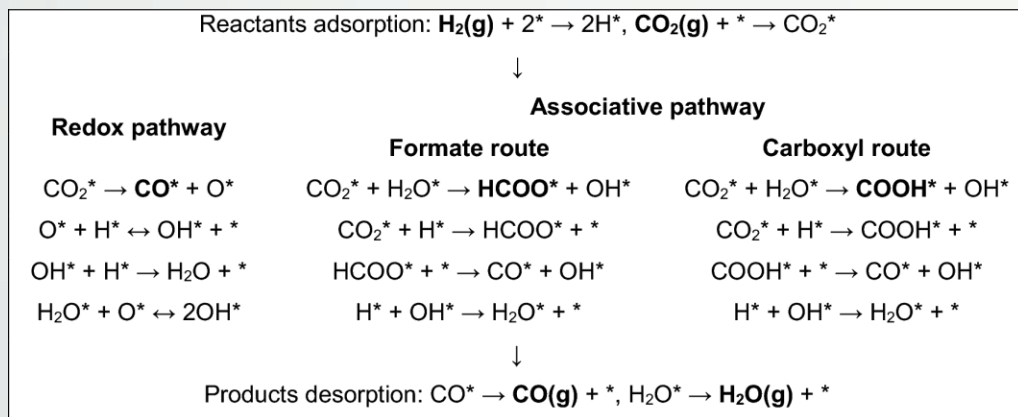


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RWGS – the influence of the support on the mechanism



- Two mechanisms proposed for the production of CO via the **RWGS**.
- **Associative mechanism** = dissociated H_2 species are involved in the formation of the carbon-containing intermediates, namely, formates, and carboxyls

Figure 8. Schematic of the redox and associative mechanism of the RWGS.¹⁰

Redox mechanism = CO_2 is reduced at surface of an electron donating catalyst (either by a metal or an oxygen vacancy of a reducible oxide) and the catalyst itself is oxidised.¹⁰

Dominant pathway depends intrinsically on catalyst composition and reaction conditions.

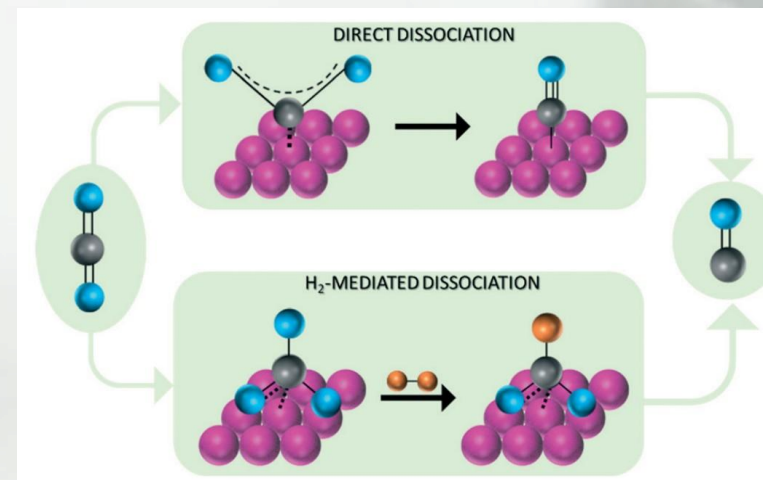


Figure 9. Schematic of direct and H-mediated mechanisms of the RWGS.¹⁰

10. F. M. Pinto, V. Y. Suzuki, R. C. Silva and F. A. La Porta, *Front Mater*, 2019, 6.



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Oxygen storage capacity – Ceria Zirconia as an ‘active support’

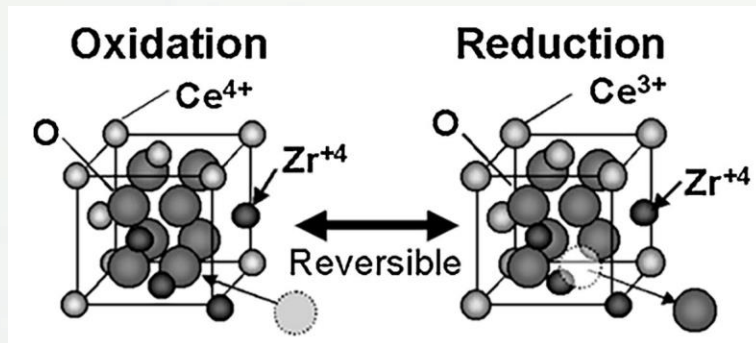


Figure 9. Representation of the redox behaviour of Ceria zirconia.¹¹

Replacement of Ce cations with Zr cations leads to distortions in the CeO₂ lattice.

Lattice distortion causes the formation of more oxygen vacancies which contribute to RWGS activity.¹²

| Composition | Ce : Zr |
|---|---------|
| Ce _{0.75} Zr _{0.25} O ₂ | 3 : 1 |
| Ce _{0.5} Zr _{0.5} O ₂ (CZ1) | 1 : 1 |
| Ce _{0.357} Zr _{0.592} La _{0.012} Nd _{0.039} O ₂ | 1 : 1.5 |
| Ce _{0.143} Zr _{0.723} La _{0.011} Nd _{0.035} Y _{0.08} 4O ₂ | 1 : 5 |
| Ce _{0.143} Zr _{0.810} La _{0.011} Nd _{0.035} O ₂ | 1 : 5 |

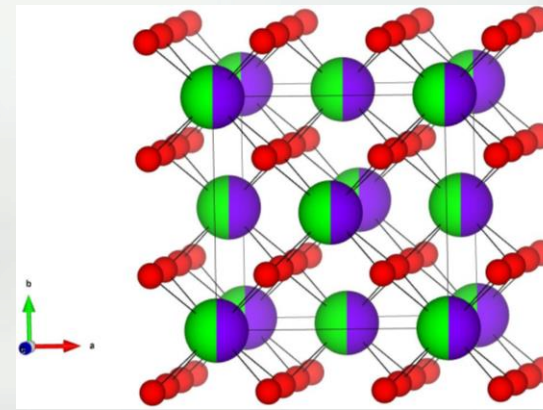
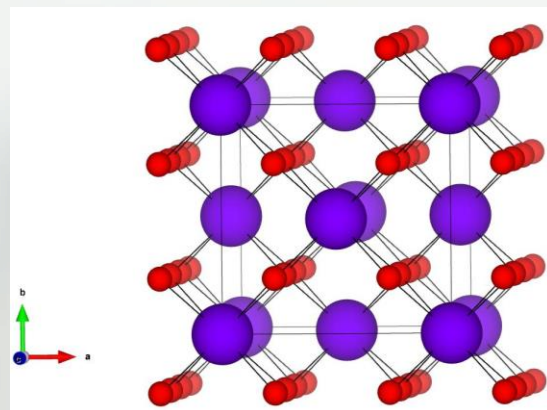


Figure 12 a) Crystal structure of CeO₂, **b)** Crystal structure of Ce_{0.5}Zr_{0.5}O_x. The positioning of cerium, zirconium and hydrogen is shown by purple, green and red respectively.

11. A. Trovarelli, Catalytic properties of ceria and CeO₂-Containing materials, *Catal Rev Sci Eng*, 1996, **38**, 439–520.

12. T. Bunluesin, R. J. Gottea and G. W. Grahamb, *Studies of the water-gas-shift reaction on ceria-supported Pt, Pd, and Rh: implications for oxygen-storage properties*, .



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Oxygen storage capacity – Ceria Zirconia composition trends

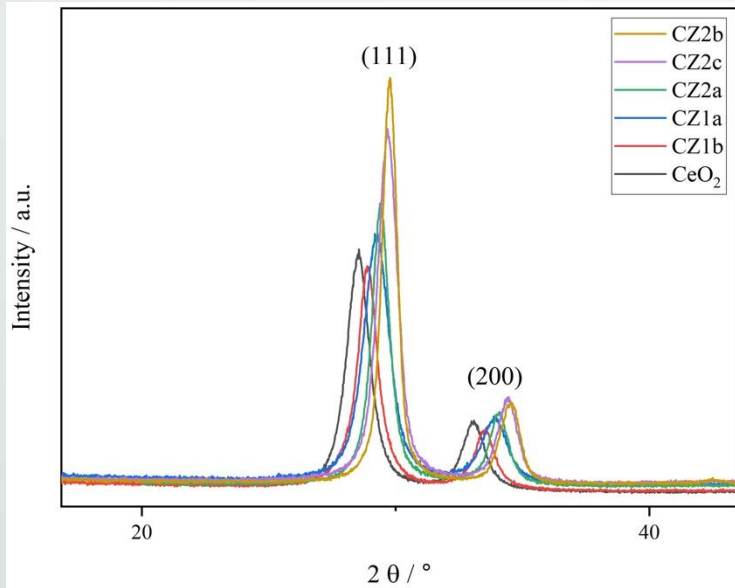


Figure 11. XRD pattern of ceria zirconia oxides with increasing Zr content zoomed on the (111) peak

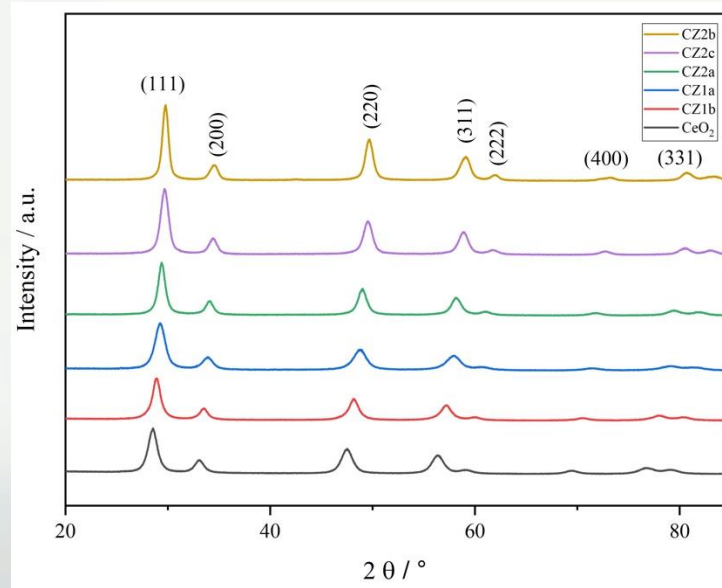


Figure 12. XRD pattern of ceria zirconia oxides with increasing Zr content.

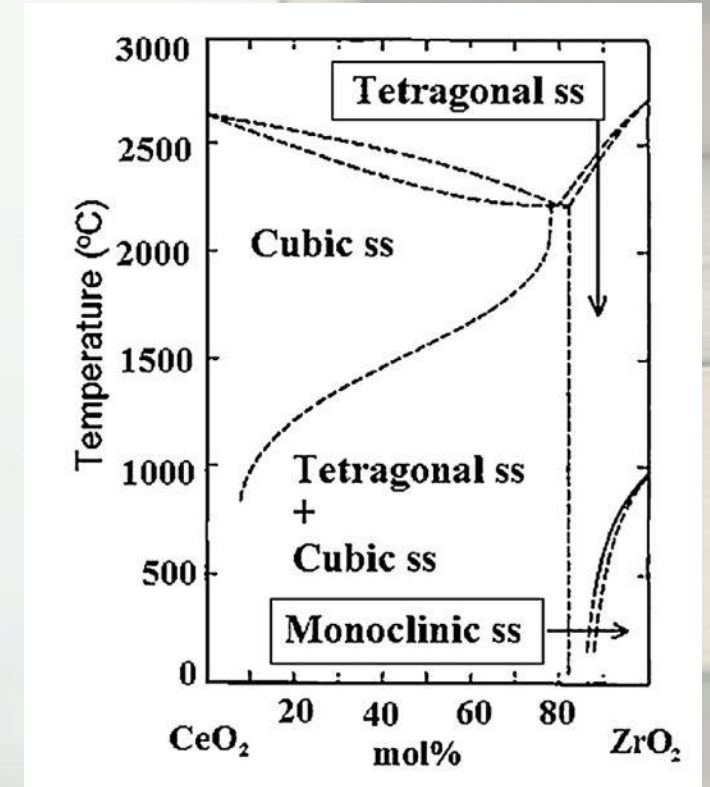


Figure 13. Phase diagram of the CeO₂-ZrO₂ system.¹³

13. F. Zhang, C.-H. Chen, J. C. Hanson, R. D. Robinson, I. P. Herman and S.-W. Chan, Phases in Ceria–Zirconia Binary Oxide (1-x)CeO₂-xZrO₂ Nanoparticles: The Effect of Particle Size, *Journal of the American Ceramic Society*, 2006, **89**, 1028–1036.



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Dynamic oxygen storage capacity measurements

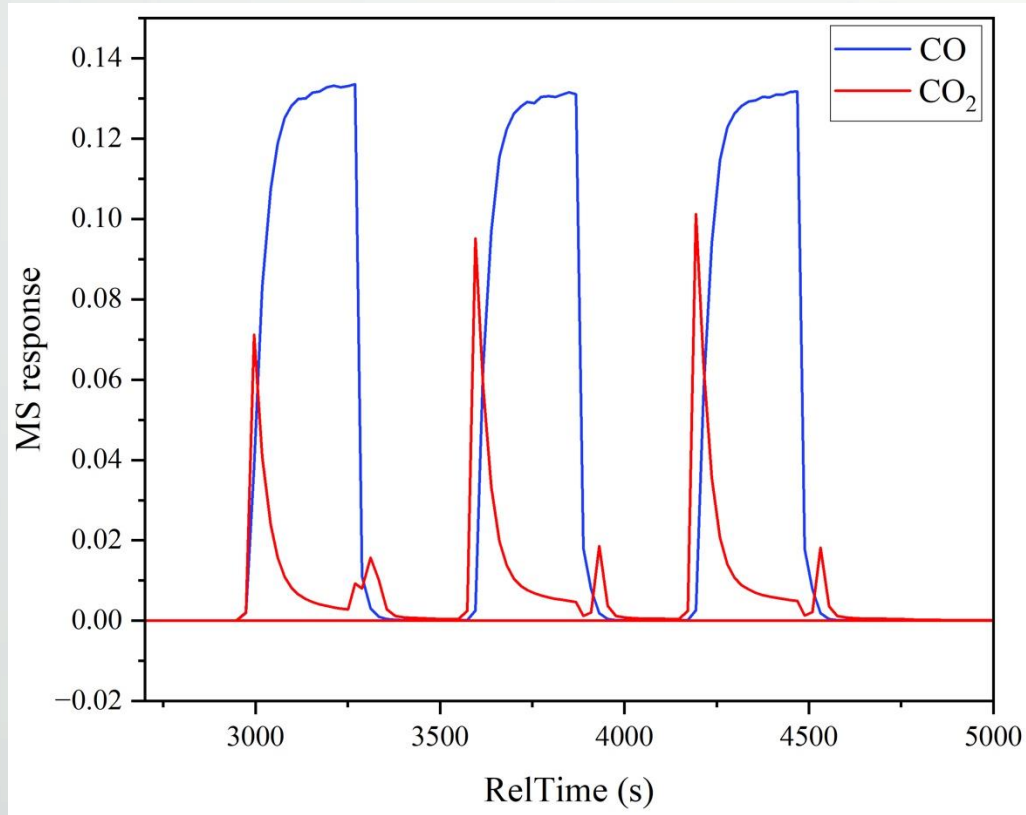


Figure 14. Raw MS response of m/z 28 (CO) and 44 (CO₂) for CZ1.

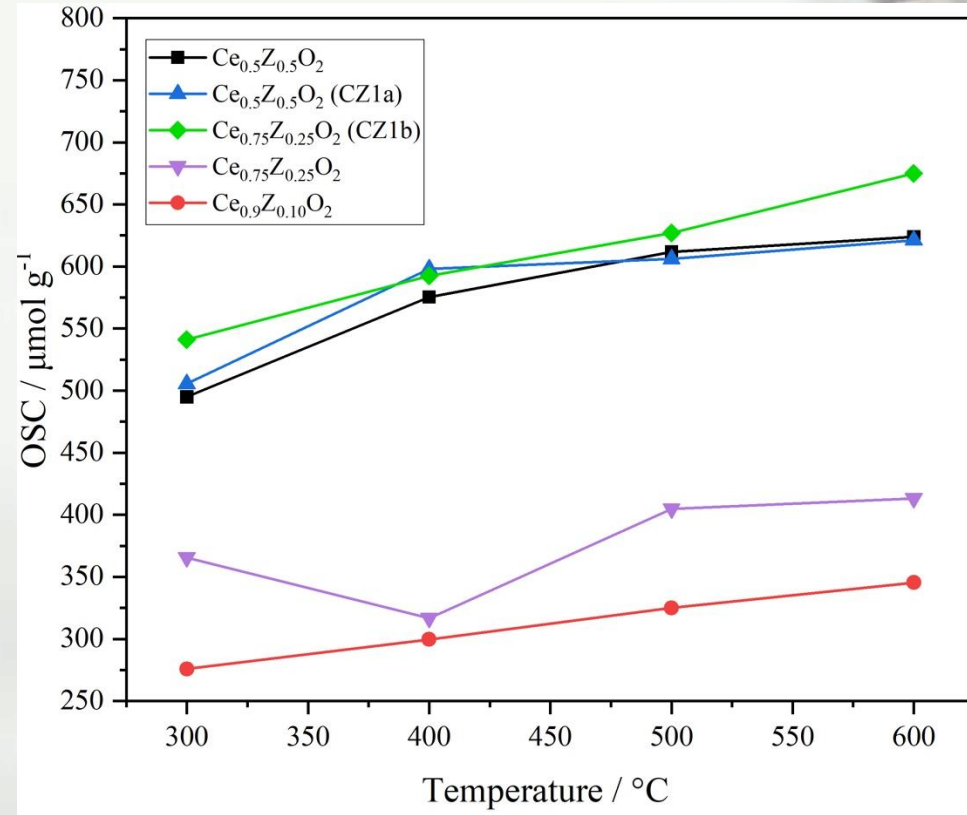


Figure 15. OSC of different compositions of ceria zirconia.



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Dynamic oxygen storage capacity measurements to elucidate kinetics

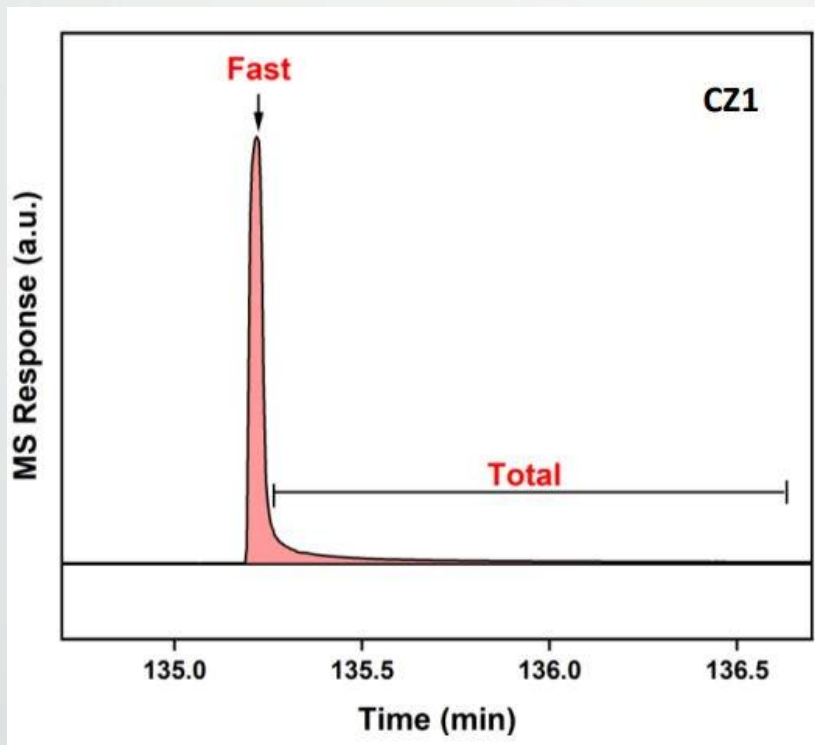


Figure 16. MS response of m/z 28 (CO₂) (CZ1).¹⁴

14. Costley-Wood, L, *Thermal Aging of Three-Way Catalysts: In Situ Characterisation Studies*, PhD Thesis, 2023

02/12/2024

- Information on kinetics and oxygen mobility of the system can be elucidated.
- Oxygen diffusion rates can be influenced by oxygen vacancy concentration and crystal structure defects.¹⁸
- Through dynamic oxygen storage testing of our mixed bare ceria zirconia supports we can measure the ‘active oxygen’ in the bulk of the ceria zirconia samples.
- Furthermore, through performing ‘fast’ and ‘total’ dynamic measurements we could investigate how the diffusion kinetics changes for samples with a higher Zr content (with more distorted crystal structures).
- Higher catalytic activity can be attributed to catalysts with increased oxygen vacancies.



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The mechanistic pathway of the RWGS is highly dependent on reaction conditions and the catalyst selected.

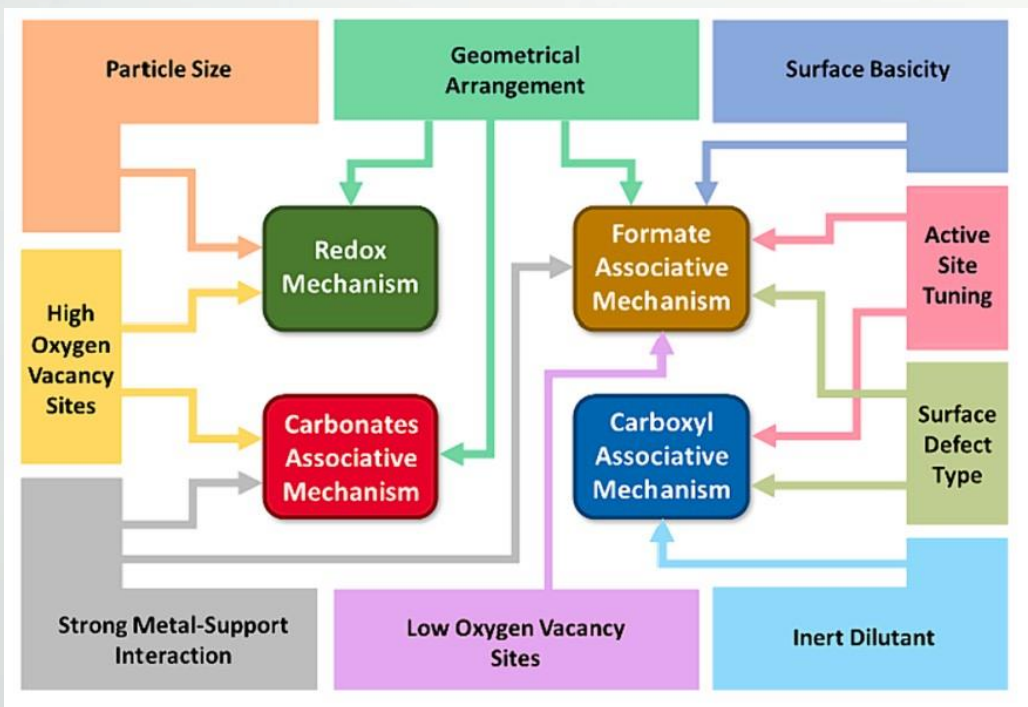


Figure 17. Factors affecting the mechanism of the RWGS.¹⁵

15. Triviño, M. L. T., Arriola, N. C., Kang, Y. S., & Seo, J. G. (2024). Transforming CO₂ to valuable feedstocks: Emerging catalytic and technological advances for the reverse water gas shift reaction. *Chemical Engineering Journal*, 487, 150369. 02/12/2024



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Techniques to extract information from a catalytic system

X-ray absorption spectroscopy: Element-specific, highly sensitive technique for structural determination.

- **XAFS** may be used to probe the local environment of a catalyst can provide an insight into the dynamics of the metal-support interface, specifically, any changes in oxidation state and coordination chemistry, as well as the formation and position of oxygen vacancies, which partly determine the high activity of reducible oxide systems in the RWGS.¹⁷

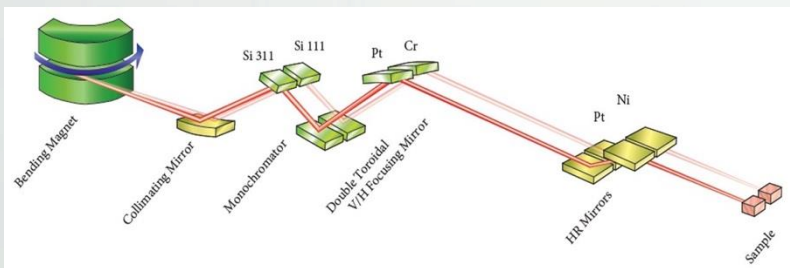


Figure 18. Diamond B18 optical layout.¹⁶

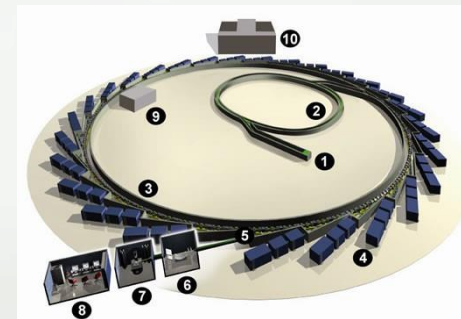


Figure 19. Schematic of the Diamond light source synchrotron.¹⁶

- **In-situ Raman spectroscopy** may be used for the identification of adsorbed species on a catalyst under operating conditions.
- Characteristic bands corresponding to vibrations associated with defects in a crystal lattice (presence / formation of oxygen vacancies) may be discerned.

16. Diamond Light Source, B18 Beamline Layout and Specifications, <https://www.diamond.ac.uk/Instruments/Spectroscopy/B18/Specification.html>

17. S. Zhao, Y. Li, E. Stavitski, R. Tappero, S. Crowley, M. J. Castaldi, D. N. Zakharov, R. G. Nuzzo, A. I. Frenkel and E. A. Stach, Operando Characterization of Catalysts through use of a Portable Microreactor, *ChemCatChem*, 2015, 7, 3683–3691.



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Advantages of a microreactor to study catalytic reactions..

- Highly controllable and reproducible environment
- Faster heat and mass transfer rates – higher SA:V ratio
- Minimized dead volume

Factors to be considered for microreactor fabrication

- Chemical compatibility
- Operating conditions
- Material transparency to technique of choice¹⁸
- Specific probing technique

Conventional cells vs microreactors

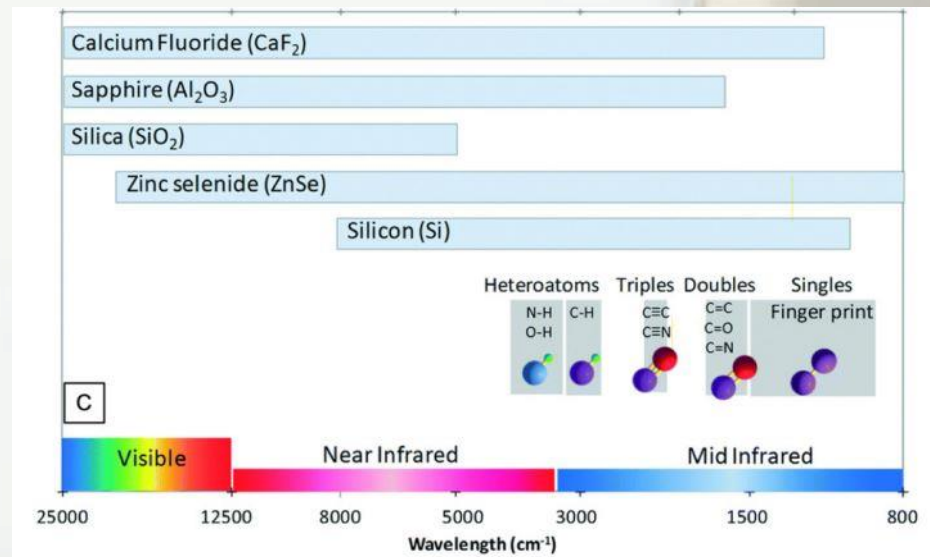


Figure 20. Light Spectrum transparency of materials which are commonly used in the assembly of microreactors.¹⁸



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A novel spectroscopic microreactor for insight into the RWGS

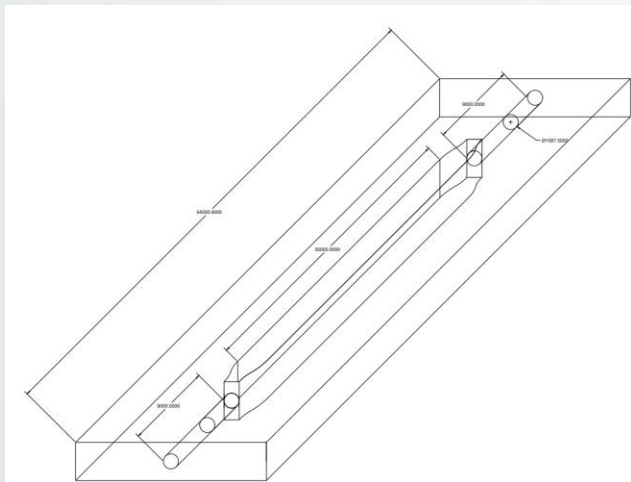


Figure 21. schematic of microreactor design

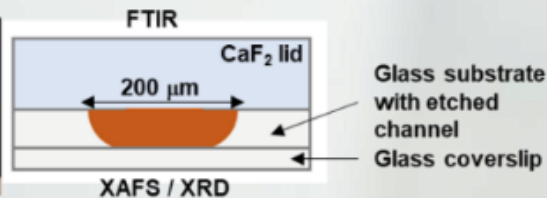


Figure 22. Conceptual representation of the catalyst bed

- Microreactor based on a ‘sandwich-like’ Calcium fluoride-quartz structure.
- Collection of XAFS or Raman from the quartz side and FTIR spectroscopic measurements through the CaF_2 side.
- we plan to test the $\text{Pt/Zr}_x\text{-Ce}_x\text{O}_{2-x}$ catalysts for the RWGS reaction in the microreactor
- Through a more reliable mechanistic and kinetic evaluation, a better understanding of the structure-performance relationship of a catalyst could be gained.
- A further understanding of the system could provide an insight into the possibilities available for improving the RWGS reaction as a practical carbon mitigation route.



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Thank you

