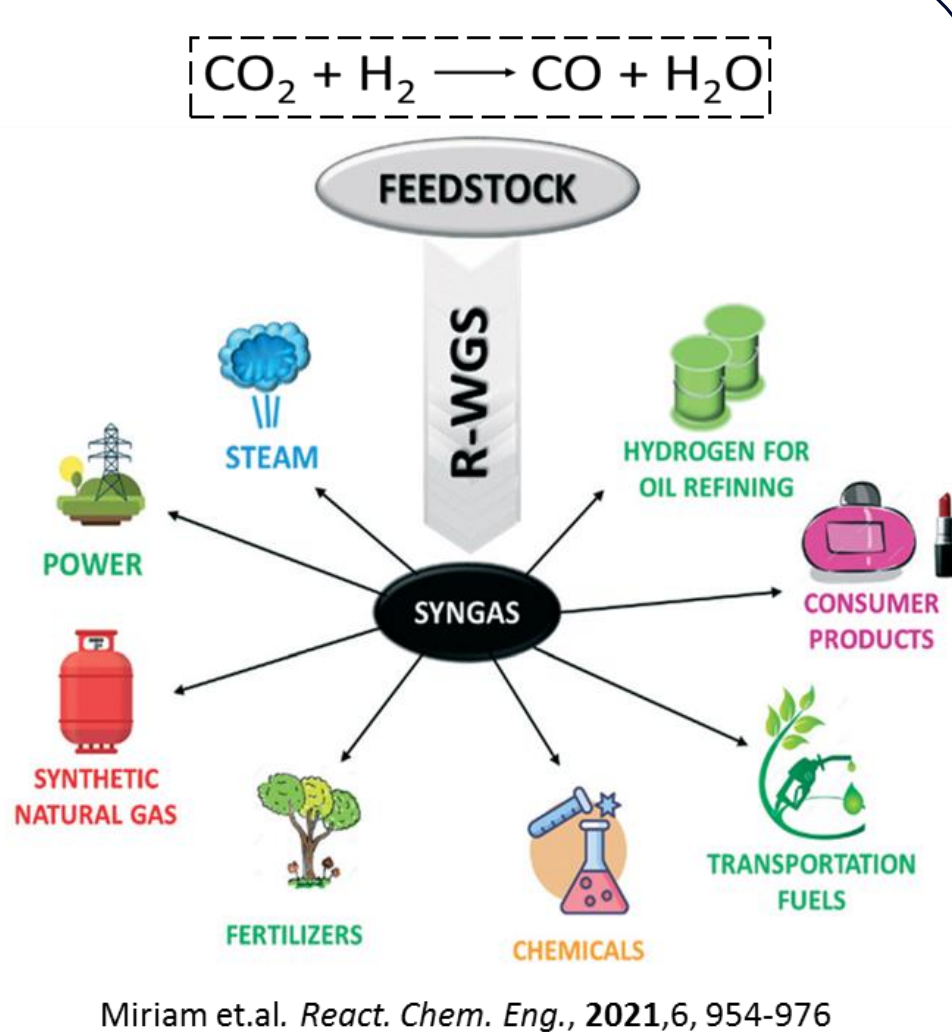


Introduction

Non-noble metal catalysts (e.g. Copper) for Carbon dioxide reduction via Reverse Water Gas Shift Reaction (RWGS) are among the most versatile, with good potential in many industrial processes. Unfortunately, the low Tamman temperature of copper and the resulting surface migration causes nanoparticles to sinter during the reaction, limiting their activity and long-term stability.¹ Inspired by our recent work² here, we asked the question of how to improve the catalytic activity and stability of Cu-catalyst using the concept of strong metal support interactions (SMSI) and defect sites cooperativity.³

A highly active and stable Cu-based catalyst for RWGS was demonstrated by creating the strong metal support interaction between Cu active sites and DFNS/TiO₂ support. The DFNS/TiO₂-Cu catalyst showed excellent catalytic performance with CO productivity of 5350 mmol g_{cat}⁻¹ h⁻¹ (i.e., 53506 mmol g_{Cu}⁻¹ h⁻¹), surpassing almost all copper-based thermal catalysts with 99.8% selectivity towards CO.



Objective and Synthesis

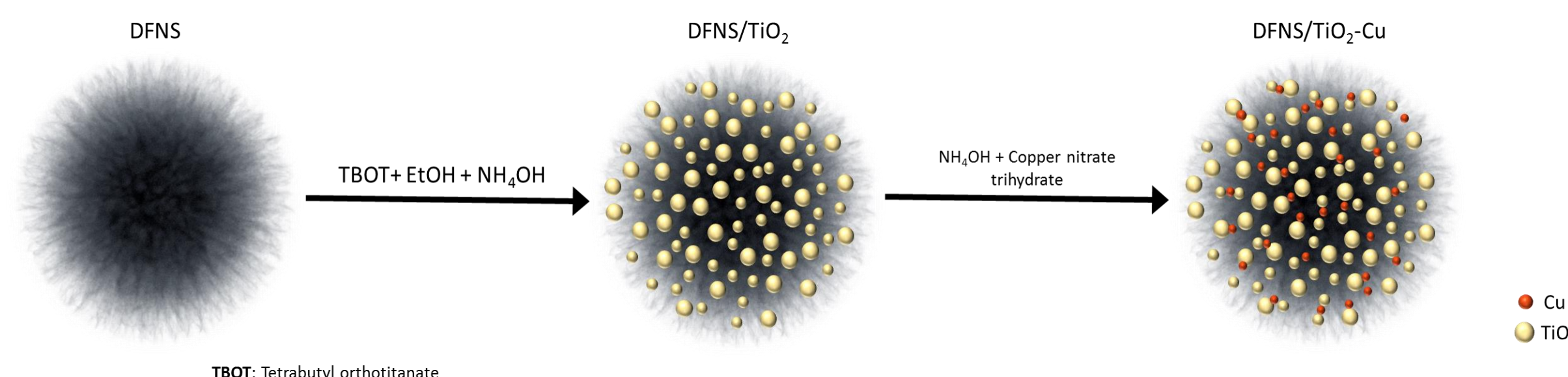
To develop a Cu-Catalyst for CO₂ Reverse Water Gas Shift Reaction (RWGS) with,

- Excellent catalytic activity
- 100% selectivity towards CO
- Long term stability

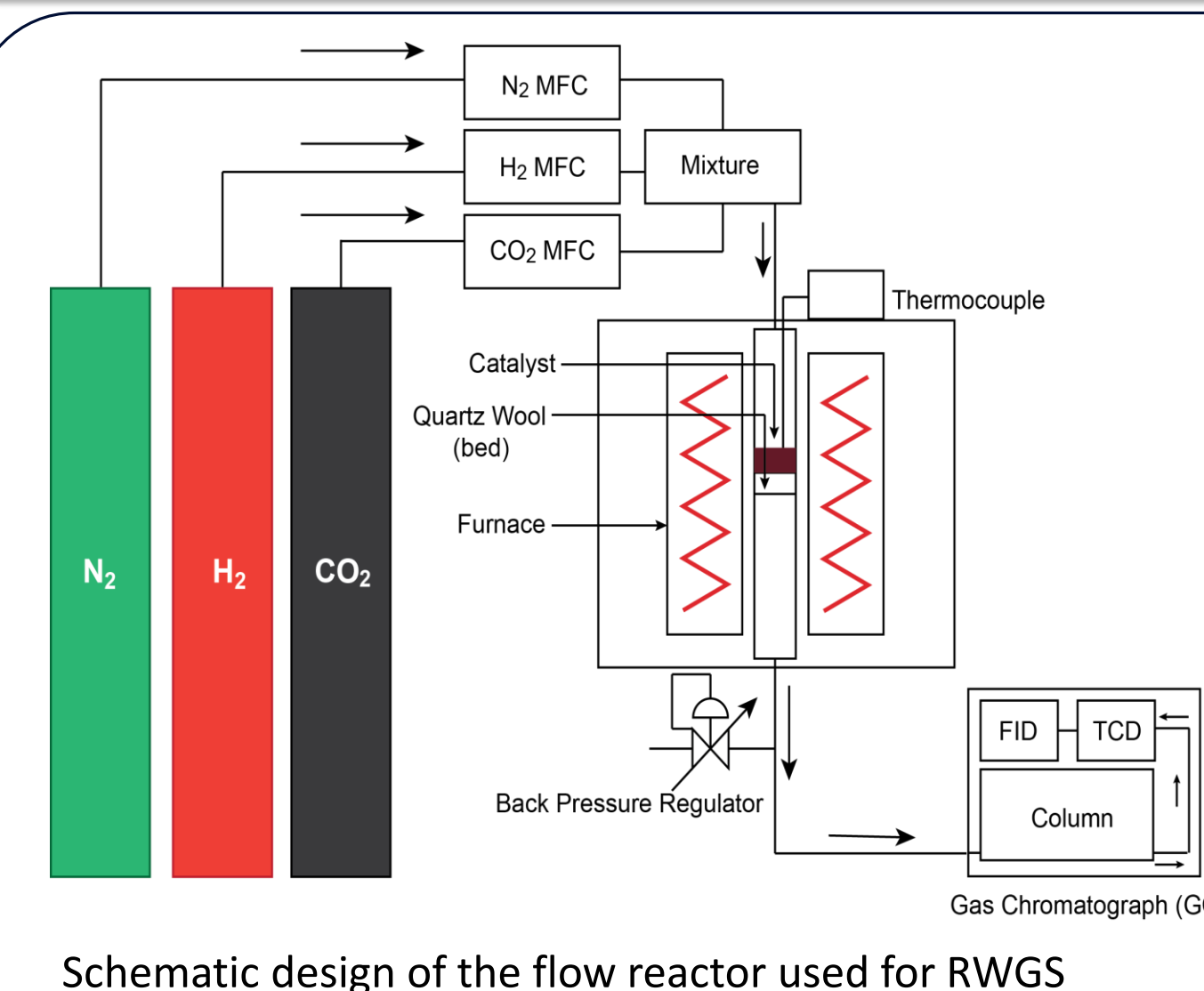
Dendritic Fibrous Nano-Silica (DFNS)⁴

- Nano-Silica (50-1200 nm)
- High surface area (1300 m² g⁻¹)
- Excellent physical and textural properties
- Thermal stability (up to 800 °C)

Synthesis of DFNS/TiO₂-Cu



CO₂ Reduction Using Fix Bed Flow Reactor



- Tube reactor was filled with DFNS/TiO₂-Cu catalyst (40 mg) and air (70 mL/min) was flowed for 2 h at 550°C. For GHSV study, the catalyst (DFNS/TiO₂-Cu) was diluted with 40 mg of SiO₂
- Catalyst was then reduced under H₂ flow (50 mL/min) for 4 h at 650°C
- CO₂ reduction was then carried out with CO₂: H₂: N₂ (40:40:1) at total flow of 81 mL/min at different temperatures (600 °C, 550 °C, 500 °C, 400 °C, 300 °C)
- Gas from the outlet was monitored by online Gas Chromatography

Acknowledgements

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We acknowledge the EM and XRD facility of TIFR, Mumbai.

Catalytic Performance of DFNS/TiO₂-Cu for RWGS Reaction

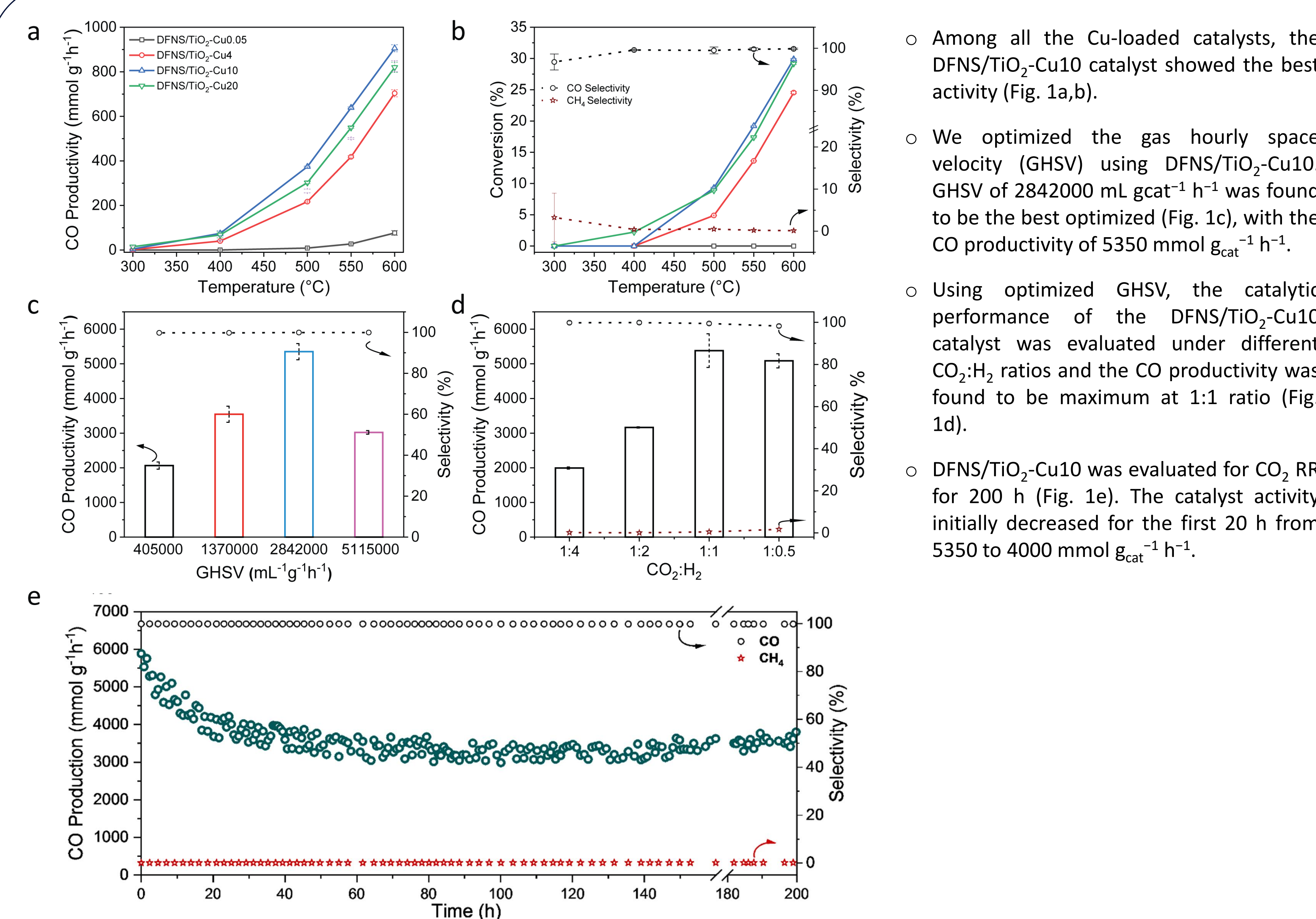


Figure 1. a) CO productivity, b) CO₂ conversion and selectivity; using DFNS/TiO₂-Cu catalysts at various temperatures, 1 bar pressure, 1:1 CO₂: H₂ ratio, and 121500 mL⁻¹ h⁻¹ GHSV; c) Effect of GHSV (using 1:1 CO₂: H₂ ratio) and d) effect of CO₂: H₂ ratio (using 2842000 mL⁻¹ h⁻¹ GHSV), on CO productivity and selectivity, at 600°C, 1 bar pressure, using DFNS/TiO₂-Cu10 catalyst; e) Long-term stability of DFNS/TiO₂-Cu10 catalyst for CO₂ to CO conversion, at 600°C temperatures, 1 bar pressure, 1:1 CO₂:H₂ ratio, and 2842000 GHSV mL⁻¹ h⁻¹.

Why DFNS/TiO₂-Cu10 is Active and Stable?

- TEM images and EDS showed uniform Cu NPs loading on DFNS/TiO₂ sphere (Fig. 2a,b,e).
- Particle size distribution of Cu NPs from 2 to 10 nm, an average particle size of around 5 nm (Fig. 2f).
- EDS mapping of the specific area in HR-TEM image was confirmed that the Cu is on the TiO₂ (Fig. 2h).
- Cu NPs underwent agglomeration and sintering and their particle size distribution changed from 2-6 nm to 2-17 nm (Fig. 3 a, d, f).
- EDS mapping indicated that the Cu NPs were still highly dispersed on the DFNS/TiO₂ support (Fig. 3e).
- Increased Cu nanoparticle size distribution could be the reason for the initial decrease in the catalytic activity in the first 20 h.

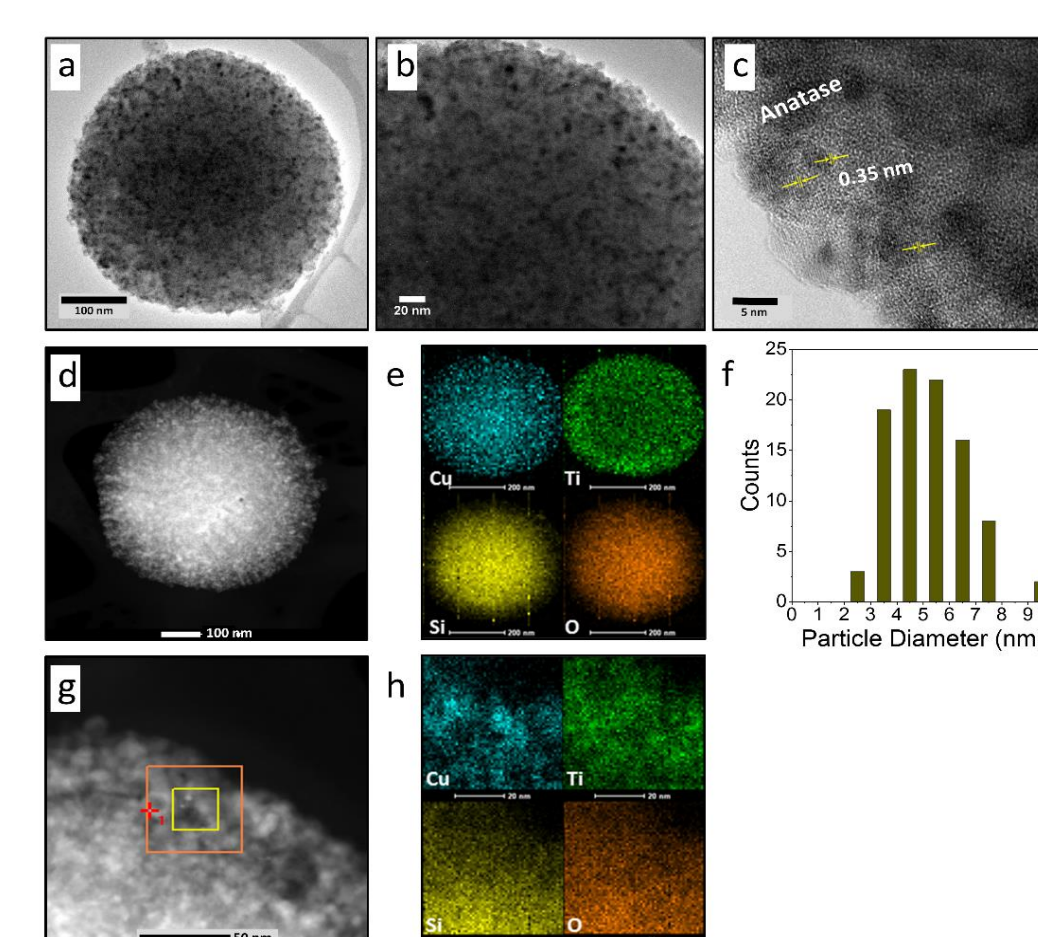


Figure 2. Characterization of the DFNS/TiO₂-Cu10 catalyst after H₂ pretreatment. a-c) HRTEM images; d,g) HAADF STEM images; f) Cu NPs size distribution; e,h) EDS element mapping;

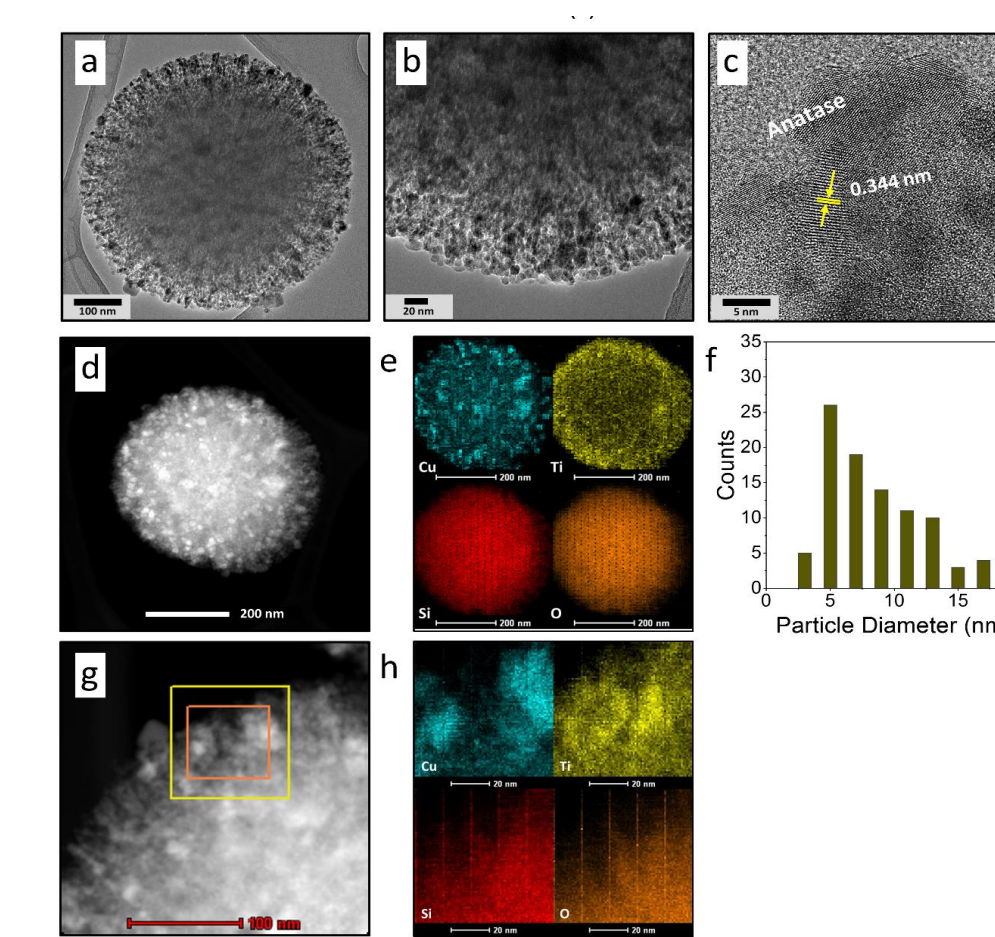


Figure 3. Structure characterization of the DFNS/TiO₂-Cu10 catalyst after 200h stability test. a,c) HRTEM images; d,g) HAADF STEM images; f) Cu NPs size distribution; and e, h) EDS element mapping of the spent catalyst.

Catalysts Comparison

DFNS/TiO₂-Cu10 was compared with some of the best-reported Cu-catalysts for CO₂ to CO conversion for CO productivity, selectivity and catalyst stability and DFNS/TiO₂-Cu10 showed the highest CO production rate and unprecedented stability compared to all reported Cu catalysts (Fig. 4).

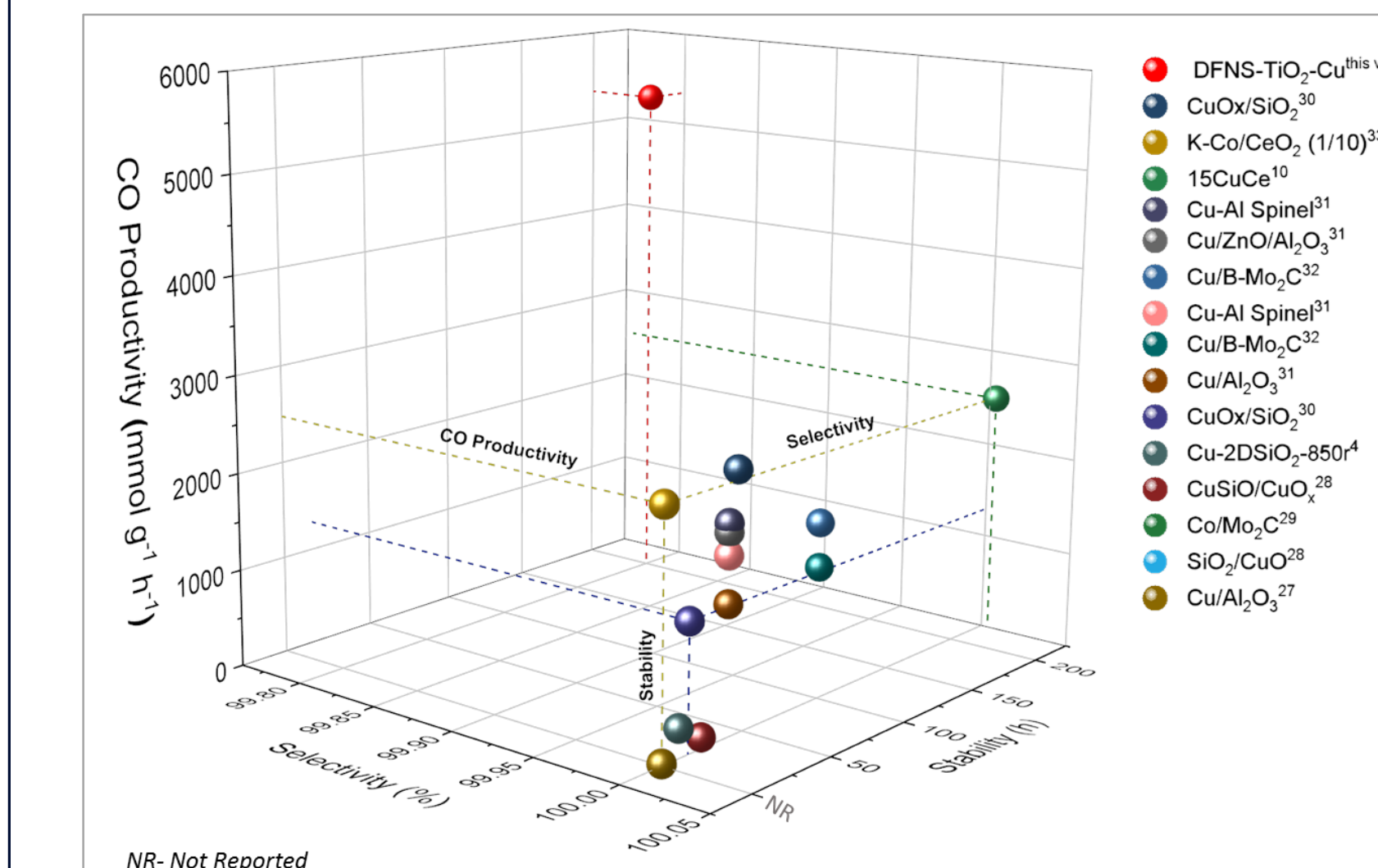
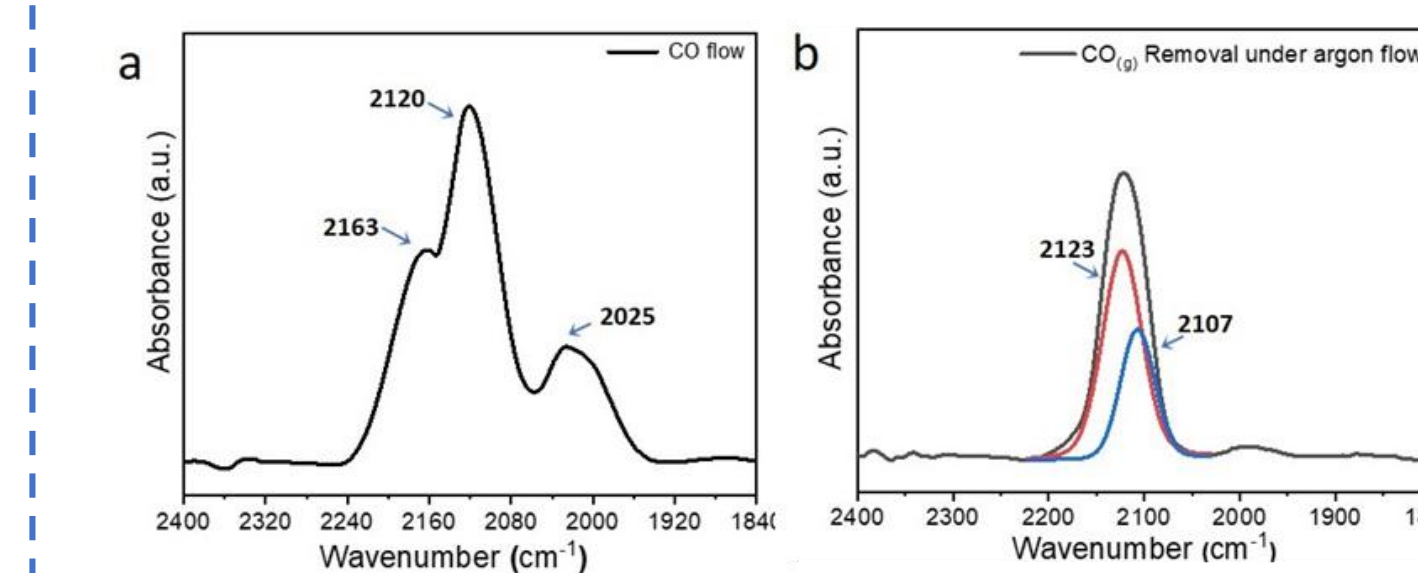


Figure 4. Comparison (CO productivity, selectivity and catalyst stability) of best reported Cu-catalytic systems for CO₂ to CO conversion

SMSI & Role of Oxygen Vacancy

The in-situ DRIFTS indicated a strong interaction between Cu and the Ti³⁺ sites, which ensured good stability and dispersion of the active copper sites.



In-situ Raman indicated that surface oxygen vacancies were produced by hydrogen, then consumed by CO₂, and then again regenerated by hydrogen.

Figure 5. In-situ DRIFTS spectra, a) after exposing the DFNS/TiO₂-Cu10 catalyst to CO with 1 mL min⁻¹ flow at 25°C, b) after removal of gaseous CO from the reactor chamber by argon flushing; and c) In-situ Raman study various reaction conditions at 400°C.

Plausible Reaction Mechanism of RWGS

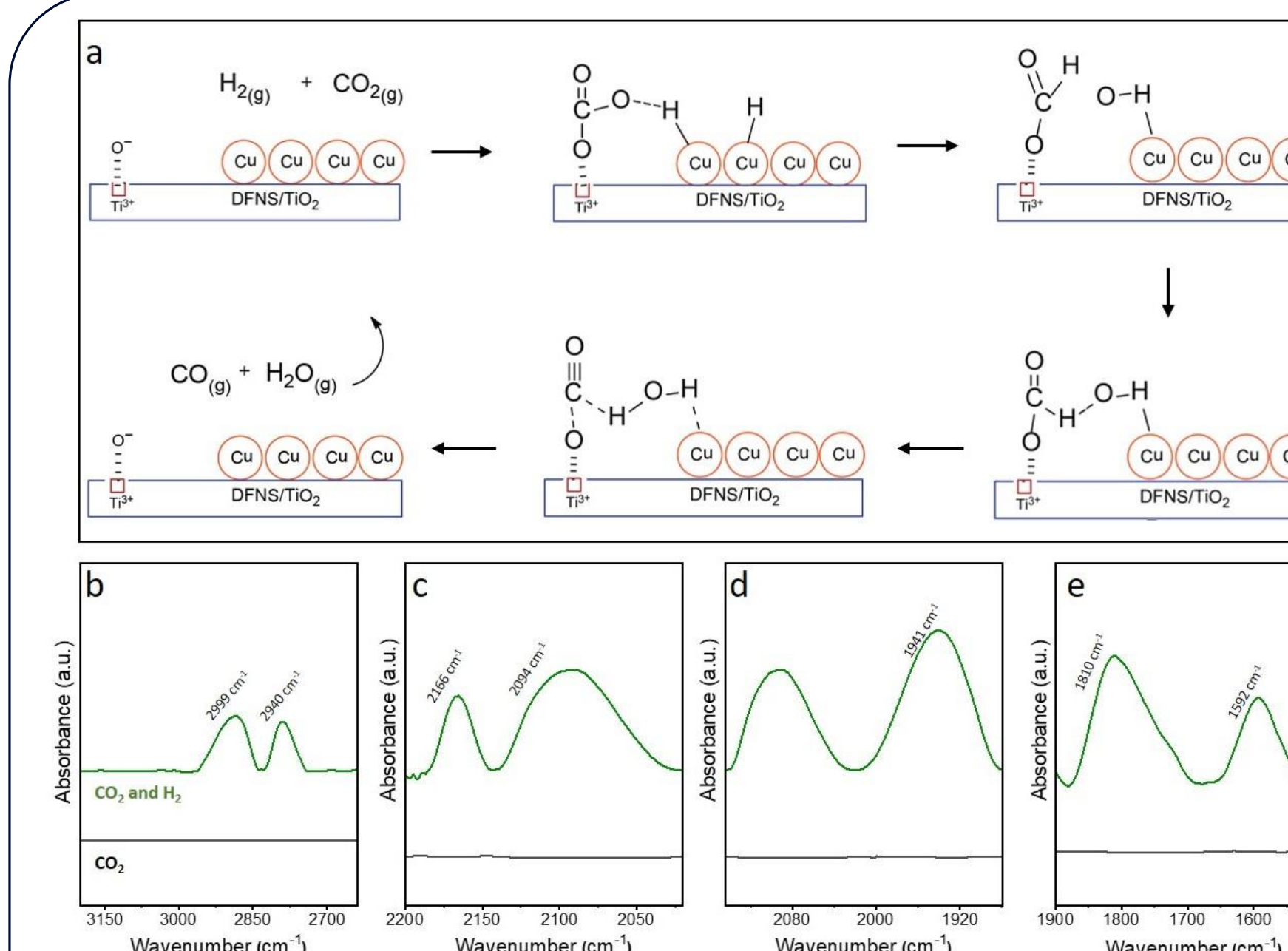


Figure 6. CO₂ to CO reduction mechanism and formation of various reaction intermediates. a) The proposed reaction pathway, and b-e) Operando FTIR spectra of DFNS/TiO₂-Cu10 catalyst during CO₂ treatment at 600°C.

Conclusions

- This catalyst showed excellent catalytic performance for CO₂ reduction with CO productivity of 5350 mmol g_{cat}⁻¹ h⁻¹ (i.e., 53506 mmol g_{Cu}⁻¹ h⁻¹), superior to all copper-based thermal catalysts. Notably, DFNS/TiO₂-Cu10 was stable for at least 200 hours.
- The strong metal-support interactions between Cu and TiO₂ kept the copper nanoparticles firmly anchored on the surface of the support.
- In-situ (DRIFTS, Raman and Operando Transmission FTIR) studies under the catalytic reaction conditions provided insights into the role of oxygen vacancies as well as indicate that CO₂ to CO conversion followed a redox pathway.

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