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Advanced membrane reactors: Water-gas shift catalyst characterisation

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Membrane assisted water-gas shift reactor

- Water-gas shift reaction (WGS): $CO + H_2O = CO_2 + H_2$ (ΔH^0 = -41 kJ/mol)
- Following coal gasification, standard desulphurisation, and pre-shift
- Reactor equipped with either a CO_2-selective or a H_2-selective membrane

- Process conditions: P = 25 bar; T = 400–450°C; H_2O/CO_{inlet} = 1.9 mol/mol; 20 ppmv H_2S
- Possible catalysts:
  - Commercial HTS (Fe_2O_3-Cr_2O_3-based) HTS1 & HTS2 (with and without CuO)
  - Commercial noble metal NM1 & NM2 (standard and sulphur tolerant)

Anticipated catalyst stability issues: redox stability and sulphur tolerance

Redox stability

HTS catalysts active as Fe_3O_4, could be oxidised (H_2 removal) or reduced (CO_2 removal):

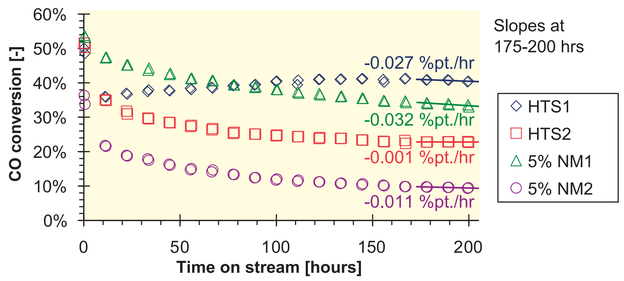
$$2\ Fe_3O_4 + H_2O = 3\ Fe_2O_3 + H_2 \qquad Fe_3O_4 + CO = 3FeO + CO_2$$

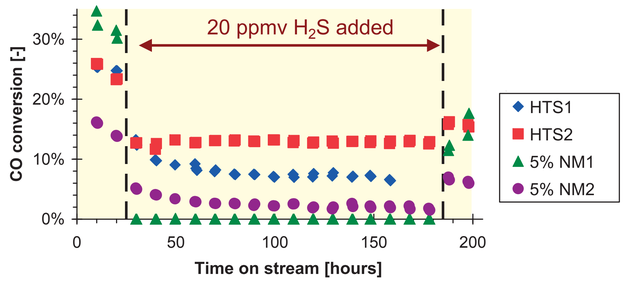
Thermodynamics predicts no stability problems even for high recovery of H_2 or CO_2 since, with H_2O/CO=2 and at 450°C:

- $[H_2O]/[H_2]$ = 113 (eq. at 99% H_2 recovery) Fe_3O_4 is stable for $[H_2O]/[H_2] < 24 \cdot 10^3$ [1,2]
- $[CO_2]/[CO]$ = 7.8 (eq. at 99% CO_2 recovery) Fe_3O_4 is stable for $[CO_2]/[CO] > 0.62$ [1,2]

Sulphur tolerance is expected to be a big issue for noble metal, not for HTS catalysts [1,3]

Stability measurements: CO conversion at 400°C





- 10% CO, 19%H_2O, 20% CO_2, 20% H_2, 31% N_2; GHSV 30,000 hr^{-1} (HTS) or 70,000 hr^{-1} (5% w/w NM diluted in alumina).
- Deactivation at 450°C, intermittently measuring activity at 400°C.
- 20 ppmv of H_2S added from 25 hours to 185 hours on stream in 2nd experiment.

Conclusions

- All catalysts deactivate in clean test.
- HTS catalysts and sulphur-tolerant noble metal (NM2) retain significant activity with 20 ppmv of H_2S.
- Poisoning is reversible as all catalysts significantly regain in activity on removal of H_2S.
- HTS2 retains a higher activity than HTS1 in the presence of H_2S, possibly due to the absence of CuO in HTS2.

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[1] Lloyd, L.; Ridler, D. E. & Twigg, M. V. (1989) Chapter 6, The Water-Gas Shift Reaction, In Catalyst Handbook, ed. M. V. Twigg, Wolfe, London, pp. 283-339.
[2] Bale, C. et al. (2007) FactSage 5.5, Thermfact / GTT-Technologies, Montreal/Aachen.
[3] Swartz, S. L. et al. (2006) Catalyst Strategies for Fuel Cells Operating with Hydrocarbon Fuels, 232nd American Chemical Society Meeting, San Francisco, CA.