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Water-gas shift for CO_2 capture in IGCC: process design and catalysis

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Introduction

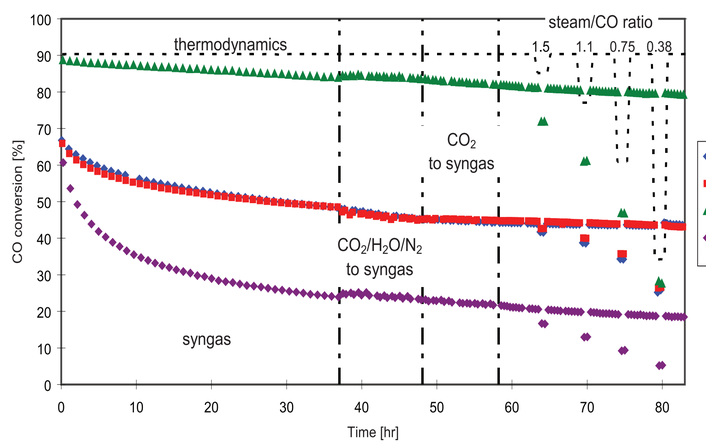
- IGCC with CO_2 capture and storage (CCS): power from coal without major CO_2 emissions – necessary part of transition to sustainable energy
- Water-gas shift (WGS) produces H_2 and CO_2 from coal syngas:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta H^0 = -41 \text{ kJ/mol}$$

- Aspen Plus: 10-15%pts efficiency penalty at 90% CO_2 capture, because of:
  1. lower heating value of the product gas
  2. separation and compression of CO_2
  3. steam demand for WGS
- Multifunctional reactors can be applied for WGS with in situ pre combustion separation of H_2 and CO_2: [1-3]
  - H_2-membrane enhanced WGS
  - CO_2-membrane enhanced WGS
  - CO_2-sorption enhanced WGS

  } WGS catalysis at atypical conditions
- Commercial catalysts: $Fe_2O_3/Cr_2O_3/CuO$ (HTS1), Fe_2O_3/Cr_2O_3 (HTS2), noble metal (NM), and sulphur-tolerant noble metal (NM-S)

Catalyst testing: CO_2 adsorption/desorption cycling



syngas (13.3%CO, 6.7%H_2, 26.7%H_2O)

alternating syngas (1 hr) / regeneration conditions (10 minutes) (23%CO_2, 26.7%H_2O)

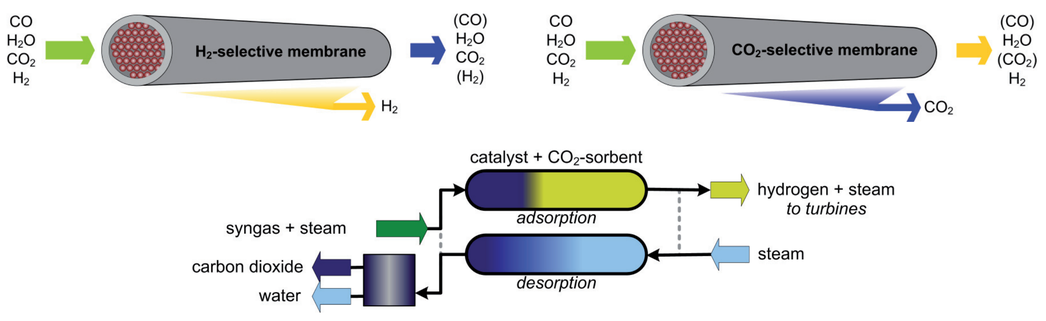
alternating syngas (1 hr) / regeneration conditions (10 minutes) (23% CO_2, 0% H_2O)

alternating syngas / syngas with decreased steam (1 hr each)

Stability at 400°C, atmospheric pressure. GHSV 30,000 hr-1 (Fe) 70,000 hr^{-1} (5%NM in Al_2O_3)

- Catalyst stability not significantly effected by regeneration conditions and no significant deactivation by lower steam content at atmospheric pressure

Multifunctional WGS reactors

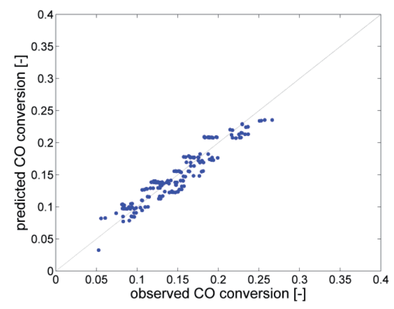


H_2-membrane/CO_2-sorption reactor: process intensification, conversion enhancement in excess of equilibrium – catalyst faces atypical conditions:

1. H_2 depletion in H_2-membrane reactor, oxidation of Fe_3O_4 at extreme recovery
2. C depletion in CO_2-membrane and sorbent reactors
3. Purge (CO_2) and regeneration (H_2O) for sorbent reactor
4. Presence of 20 ppmv of H_2S expected in IGCC

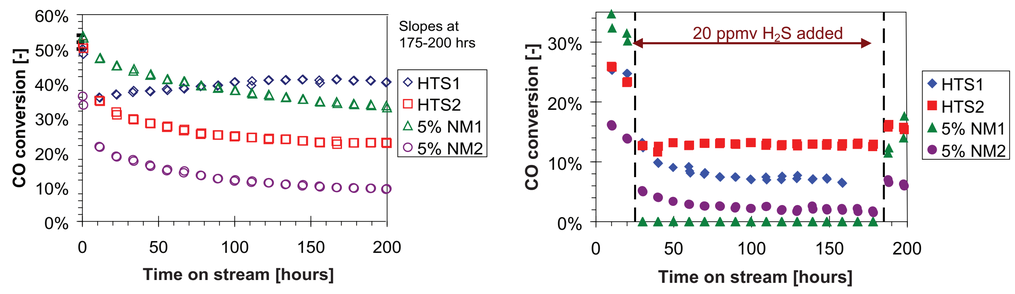
WGS intrinsic kinetics over Fe_2O_3/Cr_2O_3 in presence of H_2S

- Based on activity and stability in H_2-membrane and CO_2-membrane conditions, HTS2 selected for kinetics study with 20 ppmv H_2S
- Intrinsic kinetic data measured in microreactor system
  - 375-475°C; atmospheric pressure
  - CO 4-10% H_2O 17-23%
  - CO_2 6-36% H_2 6-36%
  - H_2S 10-30 ppmv
- Design of experiments: 2^6 +1+ extremes for CO_2 and H_2 (representing membrane effect)
- Kinetics agrees well with literature. [3]



$$R_{CO} = k_\infty e^{\frac{-105\ \text{kJ/mol}}{RT}} p_{CO}^{0.9} p_{H_2O}^{0.6} p_{CO_2}^{-0.4} p_{H_2}^{0} p_{H_2S}^{-0.4} (1-\beta)$$

Catalyst testing: membrane conditions



Stability at 450°C, atmospheric pressure, activity measured at 400°C. Left: no H_2S, H_2O/CO=1.9. Right: H_2S, H_2O/CO=1.8. Dry feed: 12%CO, 25%CO_2, 25%H_2 in N_2; GHSV 30,000 hr^{-1} (Fe) 70,000 hr^{-1} (5%NM in Al_2O_3)

- HTS2 activity is lowered by H_2S, yet less than for HTS1
- NM is very active in clean WGS, but completely poisoned by H_2S
- NM-S retains significant activity with H_2S, but is less stable than HTS_2
- All catalysts significantly regain activity upon removal of H_2S feed

Conclusion

- CCS causes an IGCC energy efficiency penalty of 10–15%-pts.
- Multifunctional reactors, integrating WGS with H_2/CO_2 separation, offer the possibility of process intensification and conversion enhancement, however involve atypical process conditions for WGS catalyst.
- Fe_2O_3/Cr_2O_3 more S-tolerant than $Fe_2O_3/Cr_2O_3/CuO$ with 20 ppmv H_2S
- Sulphur-tolerant noble metal WGS catalyst may be a suitable alternative to Fe-based catalysts.
- Catalyst stability not significantly effected by regeneration conditions and no significant deactivation by lower steam content at atmospheric pressure.
- WGS intrinsic kinetics were determined, in line with literature.
- Additional tests at elevated pressure required to verify the experimental results at realistic operating pressures.

[1] R. Allam, R. et al. 'Power Generation with Reduced CO_2 Emissions via the Sorption Enhanced Water Gas Shift Process', Third Annual Conference on Carbon Capture and Sequestration, Alexandria VA, USA, 2004.
[2] E. Kikuchi, S. et al., Chemistry Letters, 18 (1989), 489.
[3] Global Climate & Energy Project. Stanford University, CA (USA). 2006. (http://gcep.stanford.edu)
[4] D.S. Newsome, Catalysis Reviews: Science and Engineering, 21 (1980) 275.

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