Catalytic Removal of Oxygen and Pollutants in Exhaust Gases from Pressurized Oxy-Combustors

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Project Overview

Overall Goal:

- Develop and validate advanced catalytic materials and systems for purifying flue gas from pressurized oxy-combustion (OC) to meet CO_2 purity specifications for EOR and improve performance over 1st-generation OC

Typical flue gas composition from OC boilers [1]

Component	Composition
O_2	2.9 vol%
N_2	0.6 vol%
Ar	3.3 vol%
CO_2	63.0 vol%
H_2O	29.4 vol%
SO_2	1,000-8,000 ppmv
NO_x	~400 ppmv

CO_2 purity requirements for EOR [2]

Component	Limit
CO_2	≥95 vol%
N_2	1 vol%
Ar	1 vol%
H_2O	300 ppm wt
O_2	100 ppmv
SO_2	100 ppmv
NO_x	100 ppmv
CO	35 ppmv
H_2	1 vol%
CH_4	1 vol%
C_2H_6	1 vol%
C_3+	1 vol%

Refs: 1) Internal simulation results; 2) DOE/NETL. Quality Guidelines for Energy System Studies: CO_2 Impurity Design Parameters, August 2013.

Specific Objectives (1/1/2017 to 12/31/2019):

- Develop high-performance supported catalysts and a reverse flow fixed-bed reactor (RFFB) design for O_2 removal via direct reduction by CH_4;
- Develop multifunctional catalytic packing materials and a catalytic direct contact cooler (DCC) design for enhanced oxidation and removal of NO and Hg;
- Fabricate and test a small bench-scale RFFB and a catalytic DCC with a slipstream of flue gas from the Staged Pressurized Oxy-Combustion (SPOC) testing facility at Washington University in St. Louis (WUSTL);
- Characterize the fate and transformation of Hg, heavy metals, and major gas species in flue gas from the SPOC facility; and
- Perform a high-level techno-economic analysis for the catalytic flue gas purification technology integrated into a conceptual 550-MWe SPOC plant

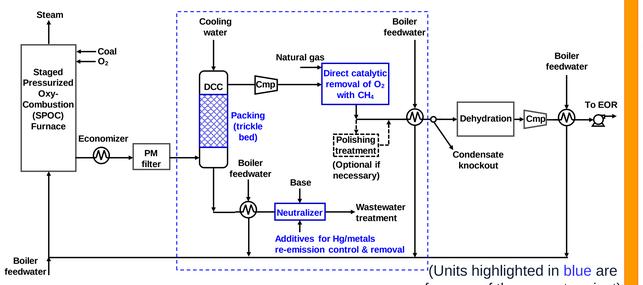
Technology Background

Technical Gaps for State-of-the-Art OC Flue Gas Purification:

- **O_2 removal**: Known commercial catalysts or scavengers are suitable only for trace amounts of O_2 (<~1,000 ppmv);
- **NO removal**: Mismatching reaction times between SO_2 and NO removal in a regular DCC (*~10 vs.100 s* for 90% removal)
- **Hg removal**: A regular DCC is not highly effective to capture elemental Hg; potential Hg reemission issue in DCC water neutralization unit (similar to a wet scrubber)
- **Hg speciation**: Emissions, fates & transformation of Hg and heavy metals are not well known for pressurized OC systems

Novel Catalytic Approaches to Overcome Technical Gaps:

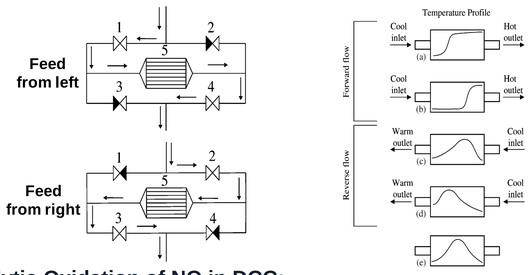
- O_2 removal via catalytic reduction
- NO/SO_2/Hg removal with catalytic oxidation



(Units highlighted in blue are focuses of the current project)

Catalytic O_2 Reduction by CH_4:

- Direct reduction of O_2 by CH_4 in a catalytic reactor avoids multiple steps and reduces operating complexity and costs
- Reaction heat recovery integrated into to the plant
- A RFFB reactor design used to maintain temperature profile by storing reaction heat and recovery for preheating feed gas



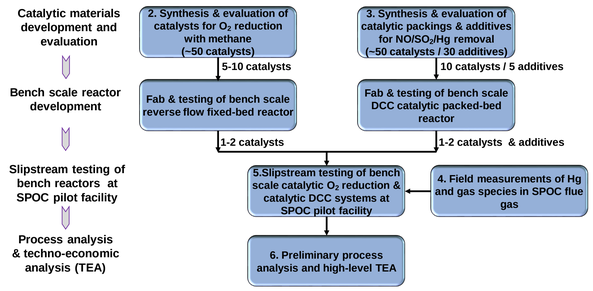
Catalytic Oxidation of NO in DCC:

- Without a catalyst, SO_2 is removed in a few seconds vs. 90% NO/NO_2 removal requires a higher pressure (15 to 30 bar) and a longer time (hundreds of seconds)

(1) $NO(g) + ½O_2(g) = NO_2(g)$ (slowest, both K_e & k_r favored at low T & high P)
(2) $NO_2(g) + SO_2(g) + H_2O(aq) = NO(g) + H_2SO_4(aq)$ (fast, Lead Chamber process)
(3) $2NO_2(g) + H_2O(aq) = HNO_2(aq) + HNO_3(aq)$ (slow, nitric acid process)
(4) $3HNO_2(aq) = HNO_3(aq) + 2NO(g) + H_2O(aq)$ (slow, nitric acid process)

- Inexpensive carbon-based catalysts used to enhance NO oxidation reaction (1) and achieve high-efficiency NO/SO_2 removal simultaneously:
  - √ A single DCC to replace two DCCs at increasing pressures
  - √ Hg removal and reemission control combined in DCC

Project Scope and Approaches



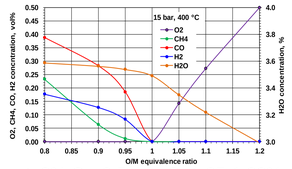
Project Progress

(1) Development of Catalysts & System for O_2 Reduction

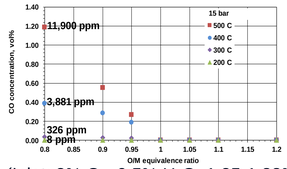
Thermodynamic Equilibria Calculations for O_2 Reduction:

(1) $CH_4 + 2O_2 = CO_2 + 2H_2O$ (complete oxidation)
(2) $CH_4 + 3/2\ O_2 = CO + 2H_2O$ (partial oxidation)
(3) $CO + 1/2\ O_2 = CO_2$ (CO oxidation)
(4) $CH_4 + H_2O = CO + 3H_2$ (CH_4 wet reforming)
(5) $CH_4 + CO_2 = 2CO + 2H_2$ (CH_4 dry reforming)
(6) $CO + H_2O = CO_2 + H_2$ (WGS reaction)
(7) $H_2 + O_2 = H_2O$ (H_2 oxidation)

- Near-stoichiometry conditions thermodynamically favor minimal formation of CO while few CH_4 or O_2 slips over
- CO formation highly sensitive to temperature; Low operating temperature reduces formation of CO

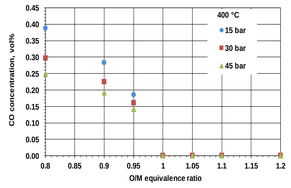


(Inlet: 3% O_2, 0.5% H_2O, 1.25-1.88% CH_4 & balance CO_2 at 15 bar & 400°C)

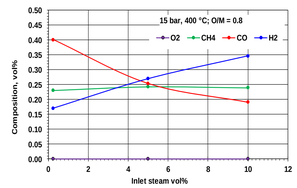


(Inlet: 3% O_2, 0.5% H_2O, 1.25-1.88% CH_4 & balance CO_2 at 15 bar)

- Increasing operation pressure slightly reduces CO formation (1/3 CO reduction by increasing pressure from 15 to 45 bar)
- Steam addition suppresses CO formation only slightly (Increasing steam from 0.25 to 10% halves CO concentration)



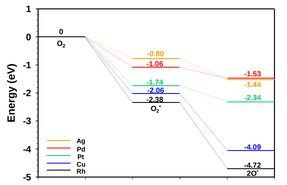
(Inlet: 3% O_2, 0.5% H_2O, 1.25-1.88% CH_4,& balance CO_2 at 400°C)



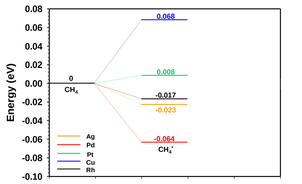
(Inlet: 3% O_2, 1.875% CH_4, 0.25-10% H_2O & balance CO_2 at 15 bar & 400°C)

DFT Calculations for O_2 Reduction by CH_4 on Metals:

- Calculations performed to identify effective metal catalysts
- O_2 dissociation is thermodynamically favorable on selected metals
- Small difference in CH_4 adsorption energy among the metals
- CH_4 adsorption energy is much larger than O_2 indicating CH_4 is more difficult to adsorb on the metal surfaces than O_2



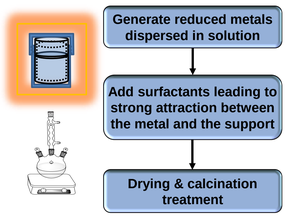
Energy diagram for O_2 dissociation on different metal surfaces



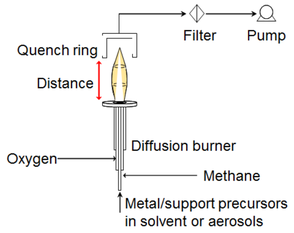
Energy diagram for CH_4 adsorption on different metal surfaces

Synthesis of Metal Catalysts for O_2 Reduction:

- Two synthesis routes used to develop metal or bimetallic catalysts on support with defined morphology
  - √ Wet synthesis - colloidal synthesis and impregnation
  - √ Gas-phase flame synthesis

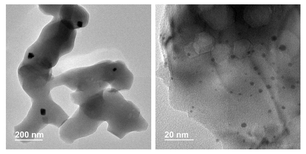


Colloidal synthesis setup

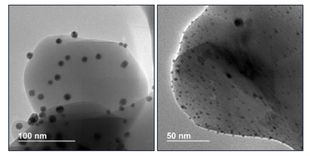


Flame synthesis setup

- Impregnation parameters (e.g., precursor, solvent, acid or base treatment of support surface, thermal treatment T) investigated to prepare >40 Pd, Cu, or PdAu alloy catalysts

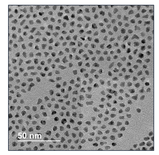


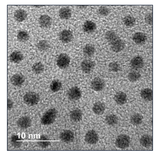
$Au/\alpha\text{-}Al_2O_3$ without (left) or with (right) surface treatment by acid: Acid treatment resulted in a uniform distribution of metal on the alumina surface due to a greater metal-surface interaction



$PdAu_3/\alpha\text{-}Al_2O_3$ thermally treated at 600°C (left) and 300°C (right): Both metal nanoparticle size and dispersion were improved at a lower temperature during thermal treatment)

- Colloidal synthesis parameters (e.g., solvent, reduction technique, surfactant) were investigated to prepare >30 Pd, Cu or PdAu alloy catalysts

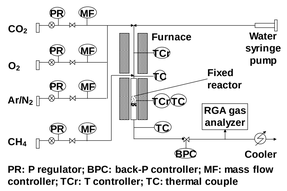




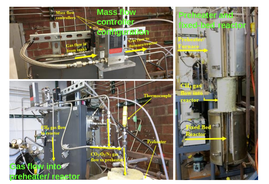
TEM micrographs of a Pd-based catalyst (left) and a Pd/Au alloy catalyst (right); uniform size of 5.6 nm for Pd and 2.7 nm for PdAu nanoparticles

Performance Screening of Metal Catalysts for O_2 Reduction:

- Activity and selectivity of synthesized catalysts are under screening evaluation
- A 0.28-in ID and 19-in long differential fixed-bed reactor (rated at 250 bar & 1,000 °F) used for the screening testing



PR: P regulator; BPC: back-P controller; MF: mass flow controller; TCr: T controller; TC: thermal couple



Schematic (a) and photograph (b) of the differential fixed-bed reactor

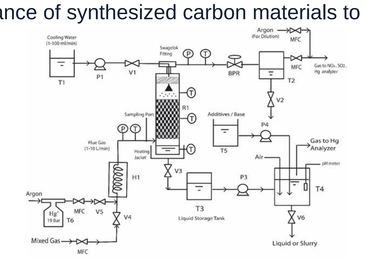
(2) Development of Catalysts & System for Enhanced NO/Hg Oxidation in DCC

Synthesis of Carbon-Based Catalysts for NO/Hg Oxidation:

- Initial efforts are focused on surface modifications for 4 commercially available granular activated carbons:
  - √ Bituminous coal-based (Filtrasorb400, Calgon Carbon)
  - √ Coconut shell-based (GC 4X8SA, General Carbon)
  - √ Wood-based (Nuchar, MeadWestvaco)
  - √ Sulfur-impregnated (GC-IPSg, General Carbon)
- Surface treatment approaches:
  - √ Introduction of N functional groups by melamine treatment
  - √ Incorporation of Cu and CeO_2 catalysts by impregnation
  - √ Growth of carbon nanofibers by C_2H_2 chemical vapor deposition on surface of carbon-Cu/CeO_2
  - √ Hydrophobic modification by introduction of silane functionalities or methyl groups

Design, Fabrication, &Testing of a Bench-Scale Catalytic DCC

- A catalytic DCC (0.5-3 inch ID by 1-2 ft length) capable of treating 1–10 SLPM flue gas under 16 bar is in progress
- Performance of synthesized carbon materials to be tested



Schematic of a bench-scale DCC packed with a carbon-based catalyst

Future Work

- Continue DFT modeling to guide catalysts development
- Synthesis optimization and screening testing of noble and non-noble metal catalysts for O_2 reduction and carbon-based catalysts for enhanced NO/Hg oxidation
- Complete design and fabrication of a bench-scale RFFB and a bench-scale catalytic DCC system and conduct testing with selected catalytic materials

Acknowledgement

DOE/NETL support thru Cooperative Agreement DE-FE0029161