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

(DOE/NETL Agreement No. DE-FE0029161)

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2018 NETL CO_2 Capture Technology Project Review Meeting

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Acknowledgements

- Project Team Members:
  - University of Illinois (UIUC):

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  - Washington University in St Louis (WUSTL):

    Pratim Biswas; Sungyoon Jung
  - AECOM:

    Bill Steen
- DOE/NETL Project Manager: Parrish Galusky, Mark Freeman
- DOE/NETL Contract Specialist: Jodi Collins

Outline

- Project Overview
- Technology Background
- Technical Approach/Project Scope
- Progress and current status of the Project
- Plans for Future Testing, Development or Commercialization

Main Objective

- 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% (min)
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.

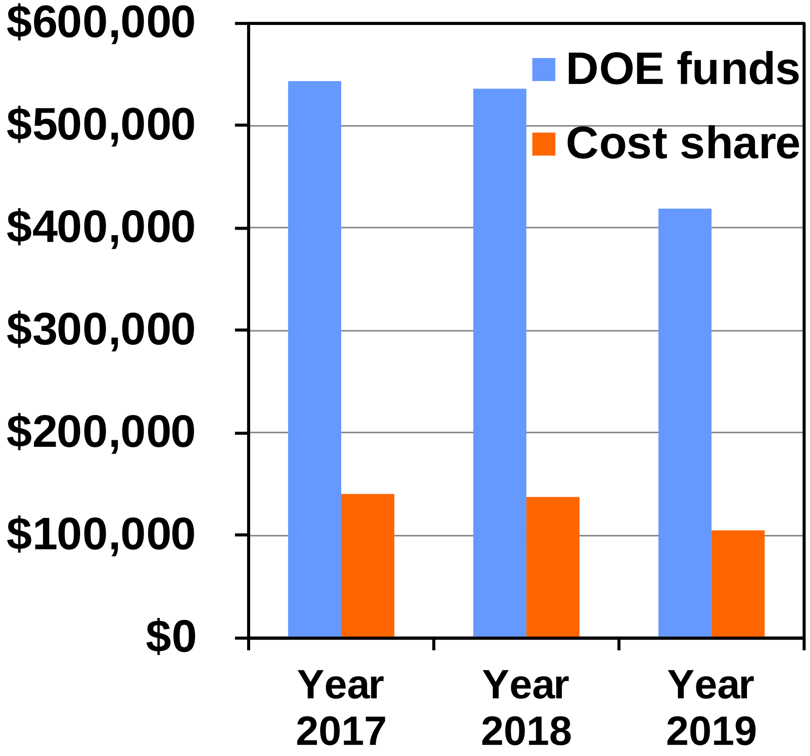
Duration, Funding and Cost Share

Project duration:

- 10/1/16–12/31/19 (39 months)
- Contract fully executed in January, 2017

Funding Profile:

- DOE funding of $1,498,323
- Cost share (in-kind) of $381,492 (20.3%)



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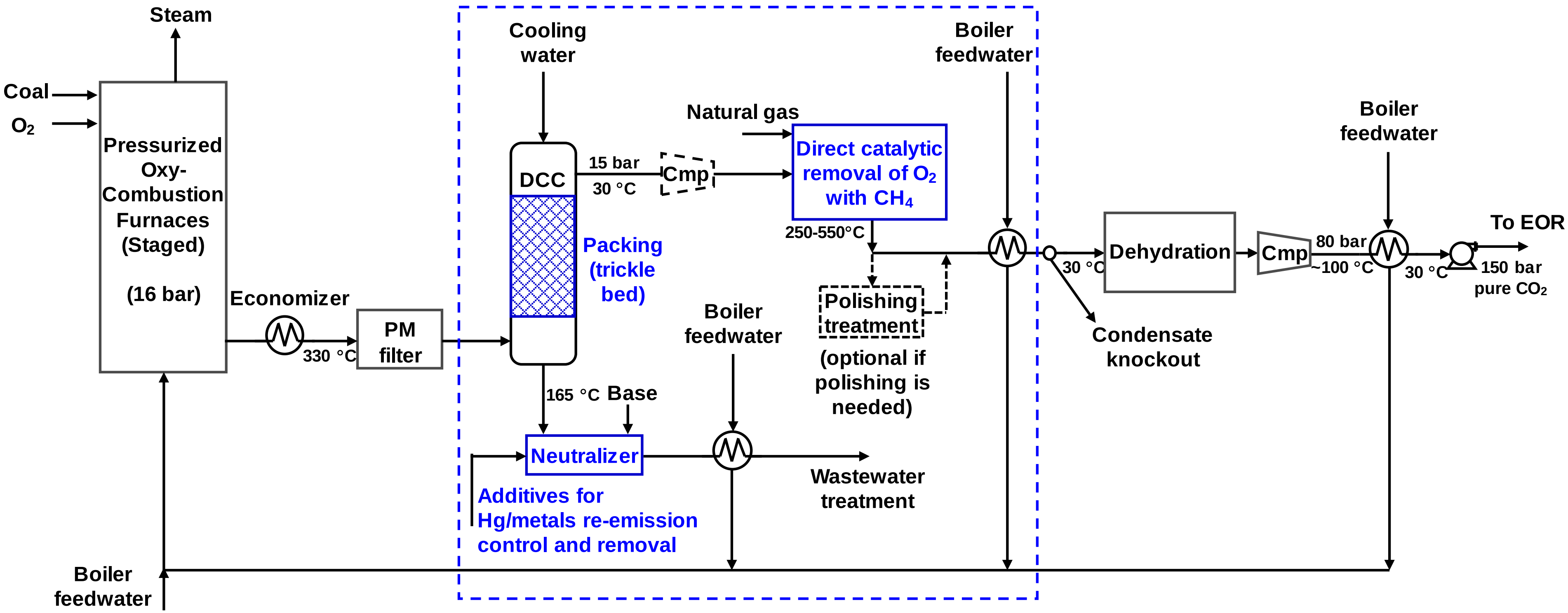
Conceptual Scheme of Flue Gas Purification Process for Pressurized OC Systems



Units highlighted in blue color are focuses of this project:

- O_2 removal with a catalytic O_2 reduction unit
- NO/SO_2/Hg removal with a catalytic direct contact cooler (DCC) unit

Technical Gaps for OC Flue Gas Purification

- **O_2 removal**: Known commercial catalysts or scavengers suitable only for trace amounts of O_2 (<~1,000 ppmv)

- **NO removal**: Mismatching reaction times between SO_2 and NO removal in a direct contact coolor (DCC)

  ~ten vs. hundreds of seconds for 90% removal

- **Hg removal**: A DCC may capture only ~15% of total 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 not well known for pressurized OC systems

Advantages Compared with Other Technologies

- Catalytic direct O_2 reduction by CH_4:
  - Direct reduction of O_2 in a single reactor

    $CH_4 + 2O_2 = CO_2 + 2H_2O$ (Complete reaction favored)
    - Avoid multiple steps (e.g., cryogenic distillation + adsorption)
    - Reduces operating complexity and CAPEX & OPEX
  - Heat recovery integrated into the power plant

- Catalytic DCC for simultaneous NOx/SO_2/Hg removal:

  $NO(g) + ½O_2(g) = NO_2(g)$ (slow, K_e & k_r favored at low T & high P)

  $NO_2(g) + SO_2(g) + H_2O(aq) = NO(g) + H_2SO_4(aq)$ (fast)

  $2NO_2(g) + H_2O(aq) = HNO_2(aq) + HNO_3(aq)$ (slow)

  $3HNO_2(aq) = HNO_3(aq) + 2NO(g) + H_2O(aq)$ (slow)

(SO$_2$ removed in seconds, then bulk NO removed;

Complete NO/NO$_2$ removal (90%) in conventional DCC requires a higher P or longer time)

  - A single device to replace 2 DCCs + 1 Hg adsorption bed
  - Inexpensive carbon-based catalysts
  - Hg reemission control in DCC water neutralization unit

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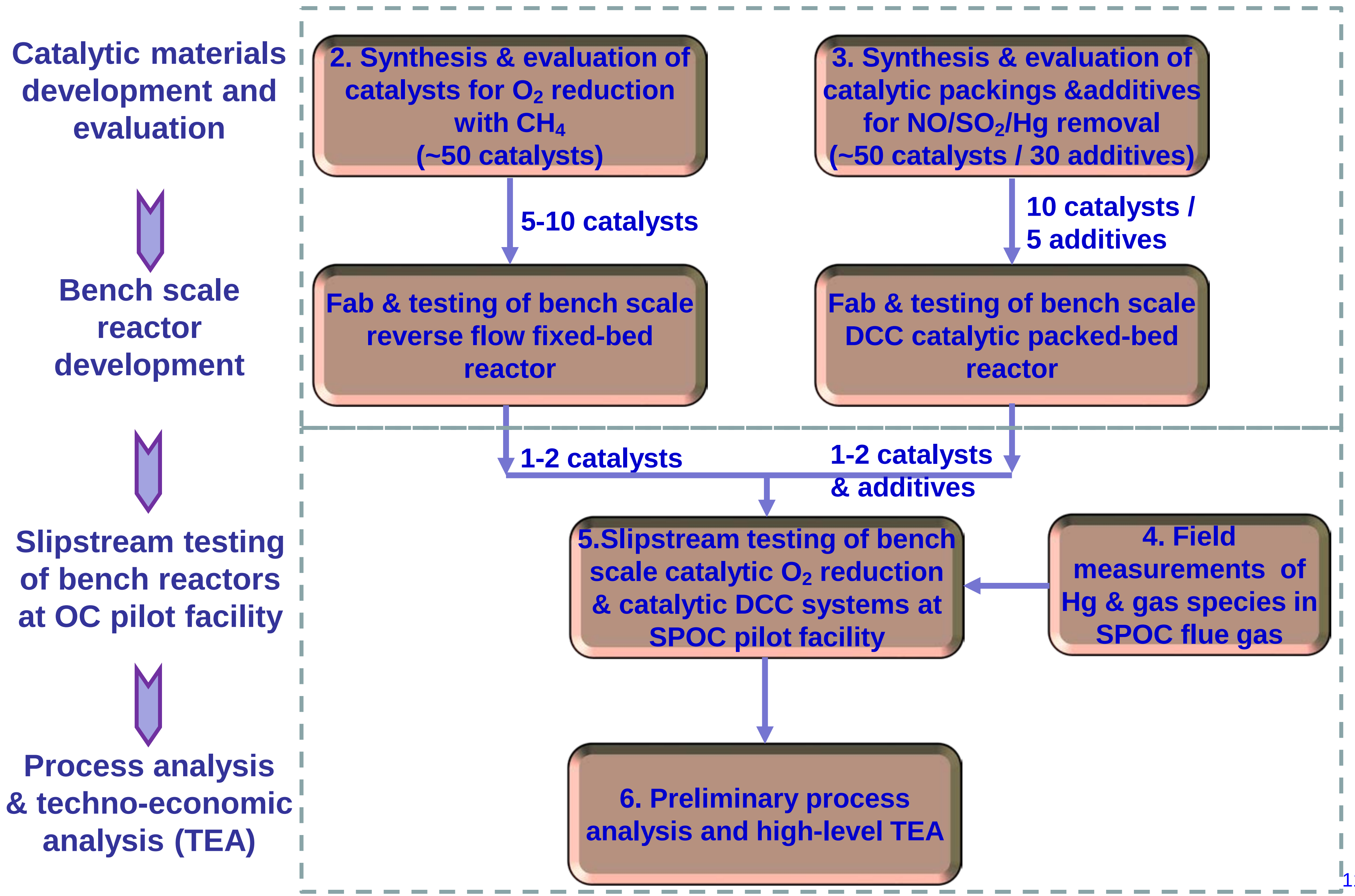
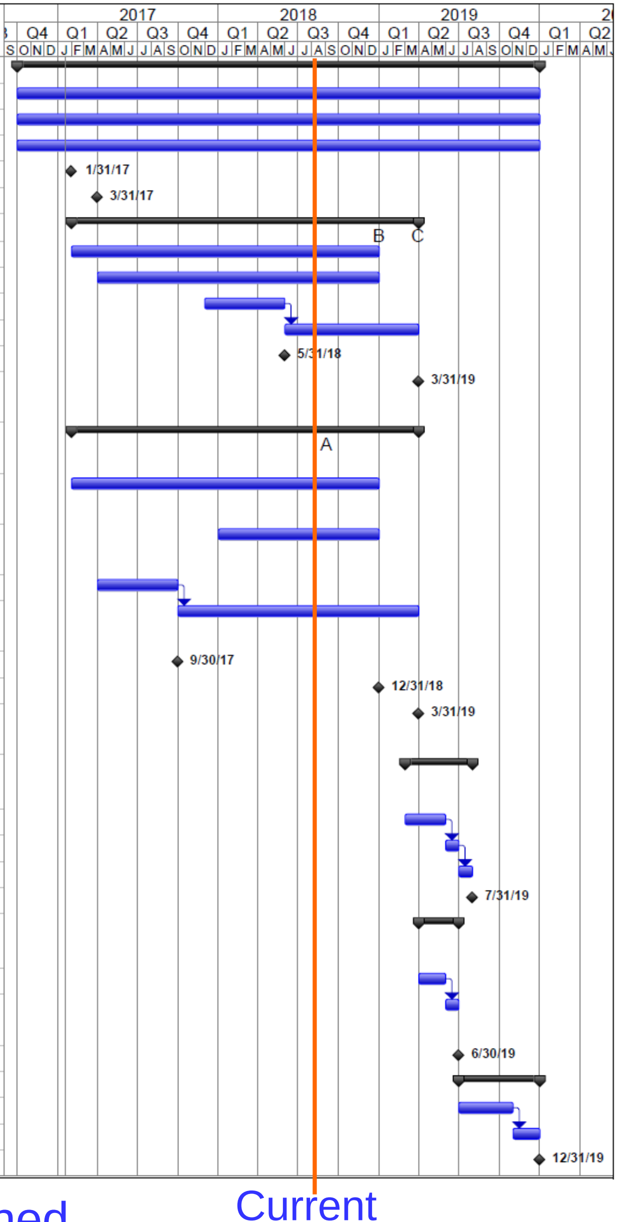
Scope of Work



Project Schedule

ID	Task Name	Start	Finish	Resource Names
1	**Task 1.0 - Project Management and Planning**	**10/1/16**	**12/31/19**	**UIUC**
2	1.1 - "Project Management & Planning" revision and updating	10/1/16	12/31/19	All
3	1.2 - Project monitoring and control	10/1/16	12/31/19	All
4	1.3 - Briefings, reports and conferences	10/1/16	12/31/19	All
5	a - Updated Project Management and Planning	1/31/17	1/31/17	
6	b - Project kickoff meeting	3/31/17	3/31/17	
7	**Task 2.0 - Catalytic Removal of Oxygen with Methane**	2/1/17	3/31/19	**UIUC**
8	2.1 - Preparation & characterization of catalysts	2/1/17	12/31/18	WUSTL,UIUC
9	2.2 - Evaluation tests of catalysts for direct O2 removal	4/1/17	12/31/18	WUSTL,UIUC
10	2.3 - Design & fabrication of a bench-scale fixed bed reactor system	12/1/17	5/31/18	UIUC
11	2.4 - Testing of the bench-scale system with selected catalysts	6/1/18	3/31/19	UIUC
12	c - A bench scale catalytic O2 removal reactor fabricated	5/31/18	5/31/18	
13	d - 1-2 catalysts identified and optimal reactor operation conditions determined	3/31/19	3/31/19	
14	**Task 3.0 - Enhanced Multi-Pollutant Control (NOx/SOx/Hg) in a Catalytic DCC**	**2/1/17**	**3/31/19**	**UIUC**
15	3.1 - Preparation & characterization of catalytic materials for enhanced NO and Hg oxidation	2/1/17	12/31/18	UIUC
16	3.2 Development & characterization of sorbents/additives for Hg re-emission control in the neutralizer	1/1/18	12/31/18	UIUC
17	3.3 - Design and fabrication of a bench scale catalytic DCC system	4/1/17	9/30/17	UIUC
18	3.4 - Parametric testing of catalytic packing materials in the bench scale DCC system	10/1/17	3/31/19	UIUC
19	e - A bench scale DCC system fabricated	9/30/17	9/30/17	
20	f - 1-2 additives/sorbents for Hg re-emission control identified	12/31/18	12/31/18	
21	g - 1-2 catalytic packing materials identified and optimal DCC operating conditions recommended	3/31/19	3/31/19	
22	**Task 4.0 - Characterization of Hg & Gas Species in Flue Gas from the WUSTL SPOC Pilot Facilities**	3/1/19	7/31/19	**AECOM**
23	4.1 - Preparation for field sampling and measurement	3/1/19	5/31/19	AECOM
24	4.2 - Field measurement at the WUSTL SPOC facilities	6/1/19	6/30/19	AECOM,WUSTL
25	4.3 - Data analysis	7/1/19	7/31/19	AECOM,WUSTL
26	h- Mercury and gas characterization results from field tests	7/31/19	7/31/19	
27	**Task 5.0 - Slipstream Testing of Bench-Scale Catalytic O2 Removal and DCC Systems at the WUSTL SPOC Pilot Facilities**	4/1/19	6/30/19	**WUSTL**
28	5.1 - Installation and tuning of bench scale systems	4/1/19	5/31/19	UIUC,WUSTL
29	5.2 - Field testing with a slipstream flue gas from the SPOC pilot facilities	6/1/19	6/30/19	All
30	I - Slipstream testing with the flue gas from the SPOC pilot completed	6/30/19	6/30/19	
31	**Task 6.0 - High-Level Techno-Economic Analysis**	**7/1/19**	**12/31/19**	**AECOM**
32	6.1 - Preliminary process analysis	7/1/19	10/31/19	All
33	6.2 - Preliminary cost analysis	11/1/19	12/31/19	All
34	j - Preliminary process analysis and cost estimation completed	12/31/19	12/31/19	



All milestones up to date have been accomplished

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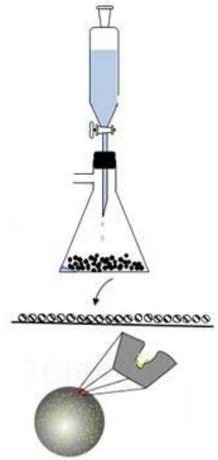
Task 2.0 Catalytic Removal of O_2 with CH_4: Synthesis of Metal Catalysts for O_2 Reduction

Two synthesis routes to develop metal or bimetallic catalysts

- Wet synthesis: impregnation and sol-gel
- Gas-phase flame synthesis

Two support materials

- Alumina
- Titania



Metal precursor solution to wet particles and fill pores

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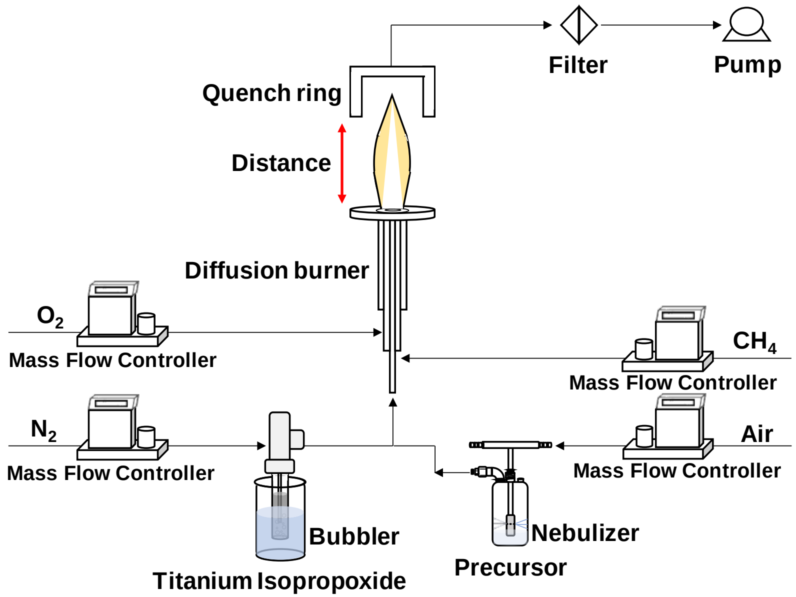
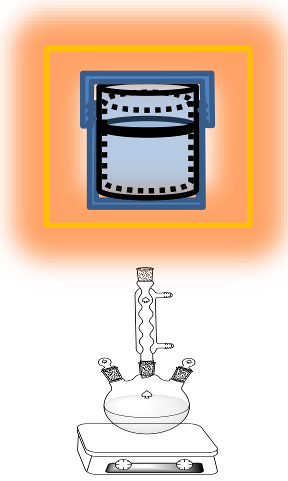
Drying, calcination and red-ox treatment to form metal oxide or metal

Incipient wetness impregnation



Flame synthesis setup



Generate sol and gel with dispersed metals

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Add additives leading to strong attraction between metal and support

↓

Drying, calcination and red-ox treatment

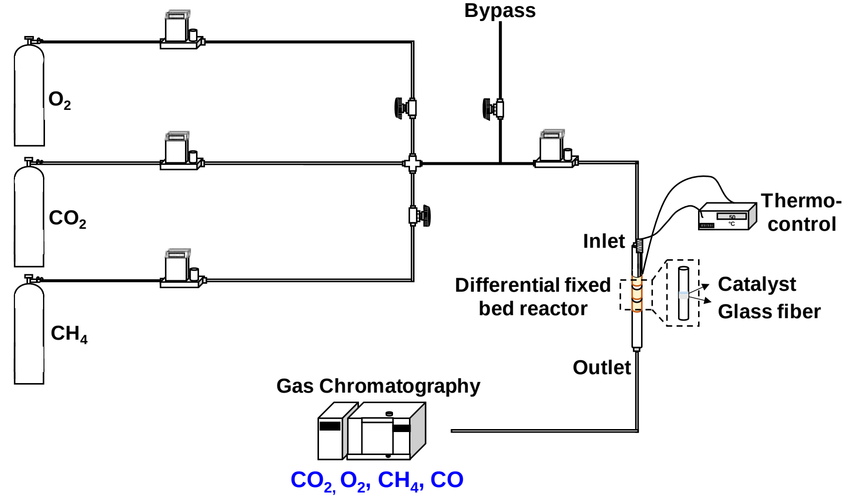
Sol-gel synthesis setup

Characterization and Evaluation of Metal Catalysts for O_2 Reduction

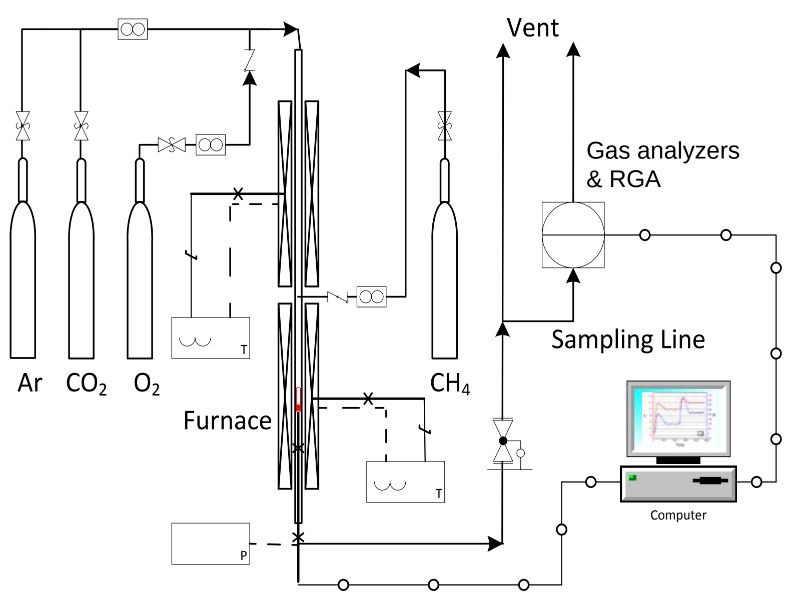
3 differential fixed-bed reactors for catalyst screening studies:

- Ambient pressure fixed-bed reactor at WUSTL
- Ambient pressure fixed-bed reactor at UIUC
- High pressure fixed-bed reactor at UIUC

0.28-in ID and 19-in long reactor rated at 250 bar @1,000 °F

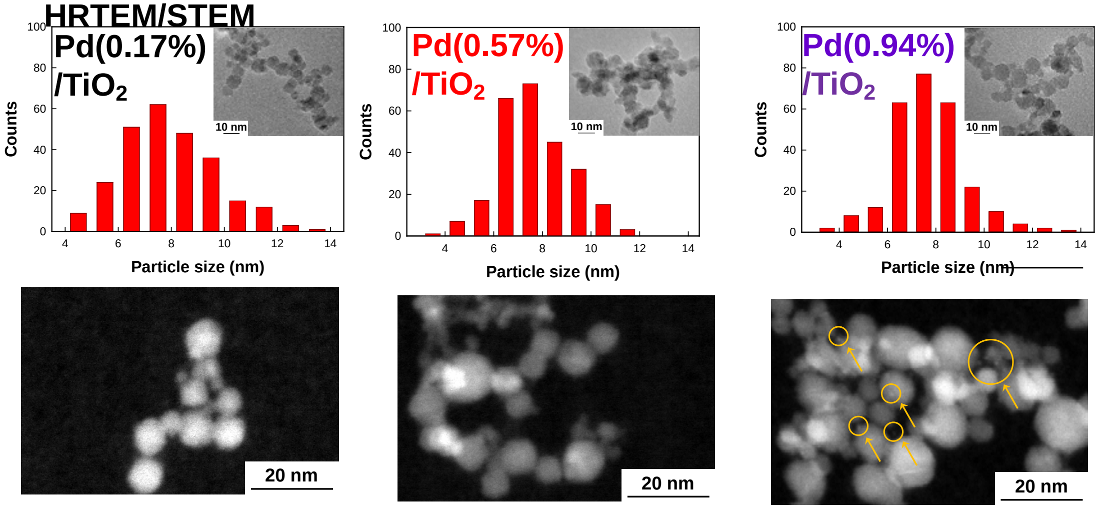


Ambient pressure fixed-bed reactor

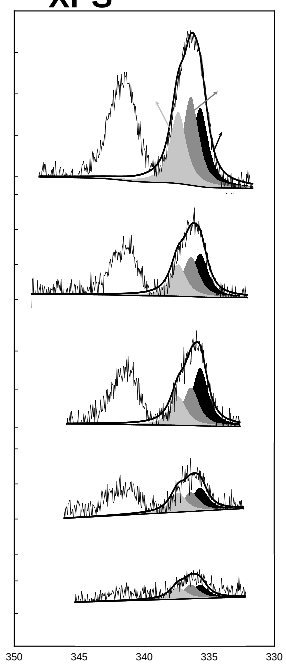


High pressure fixed-bed reactor

Baseline Catalysts Made with Flame Aerosol Technique: Pd Catalysts Supported on Titania

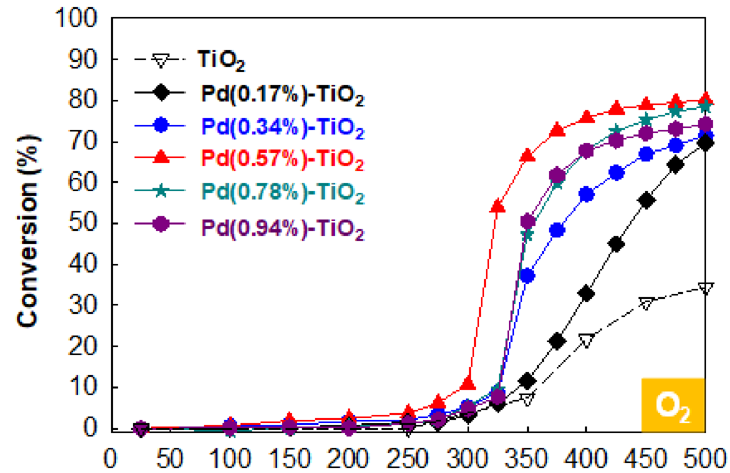


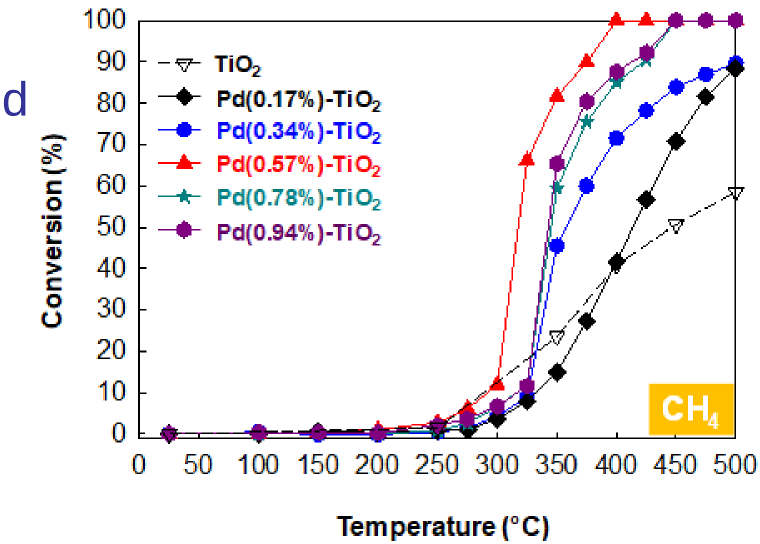
XPS



Pd (%)	PdOx (%)	PdO (%)
33	34	33
35	32	33
42	31	26
36	36	28
36	39	25

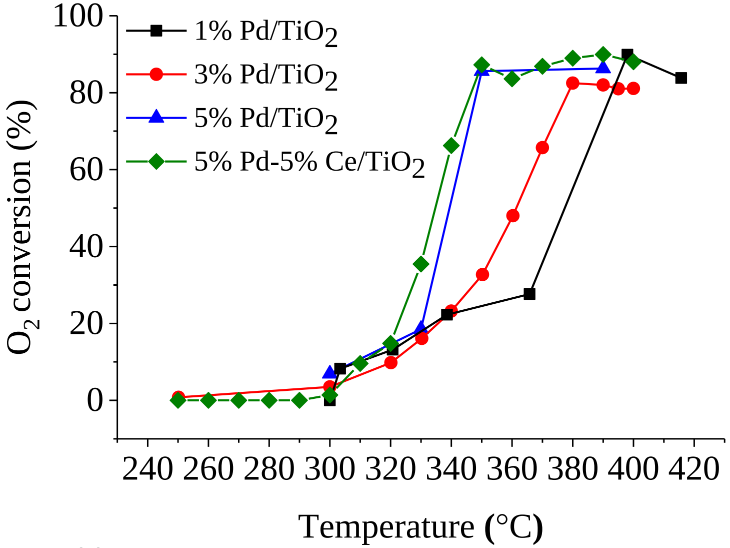
- Average particle size of ~8 nm; Sub-nano Pd clusters < 1 nm
- Highest metallic Pd% observed for Pd(0.57%)/TiO_2
- Pd(0.57%)/TiO_2 showed optimal O_2 conversion
- Higher conversion of CH_4 than O_2 indicates other CH_4 reactions

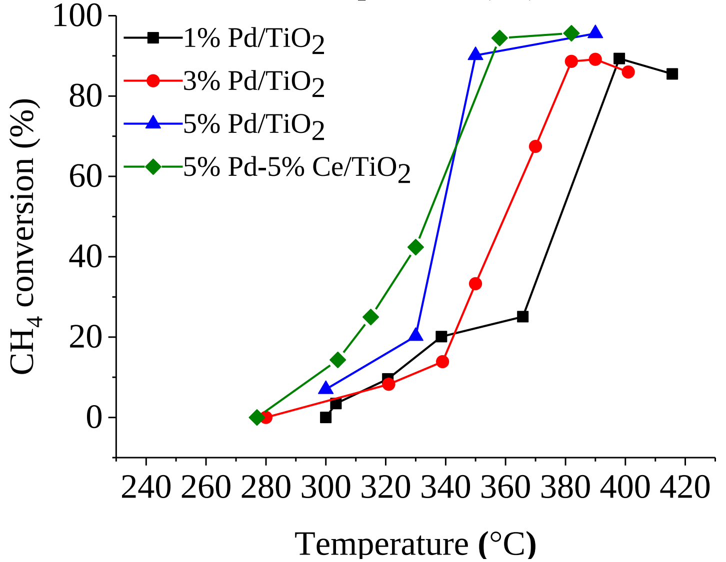




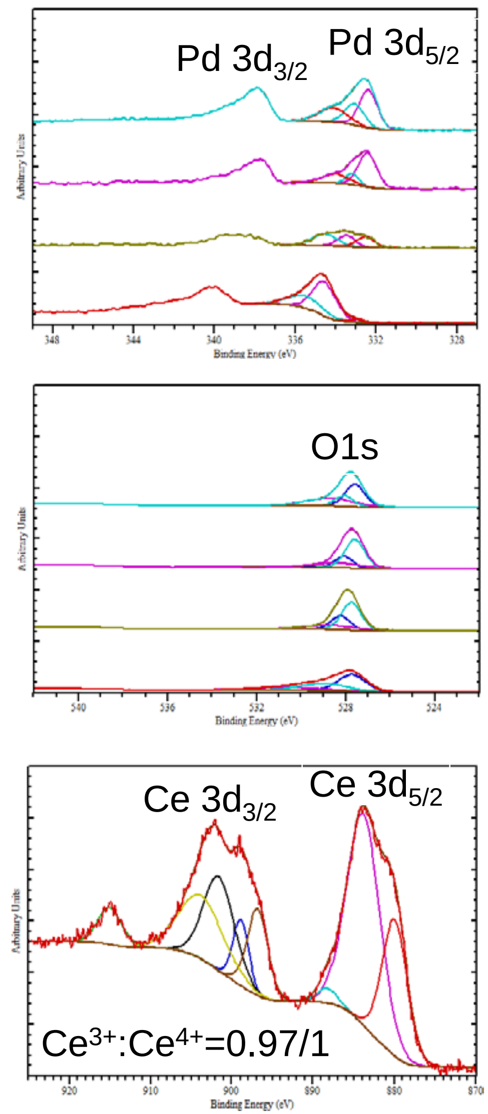
Ambient pressure; Feed gas (stoichiometric): 1.5% CH_4, 3% O_2 & balance CO_2; GHSV=19,200 hr^{-1}

Baseline Catalysts Made with Wet Chemistry Technique: Pd or Pd Composite Metals Supported on Titania





15 bar; Feed gas:1.5% CH_4, 3% O_2 and balance CO_2; GHSV=30,000 hr^{-1}



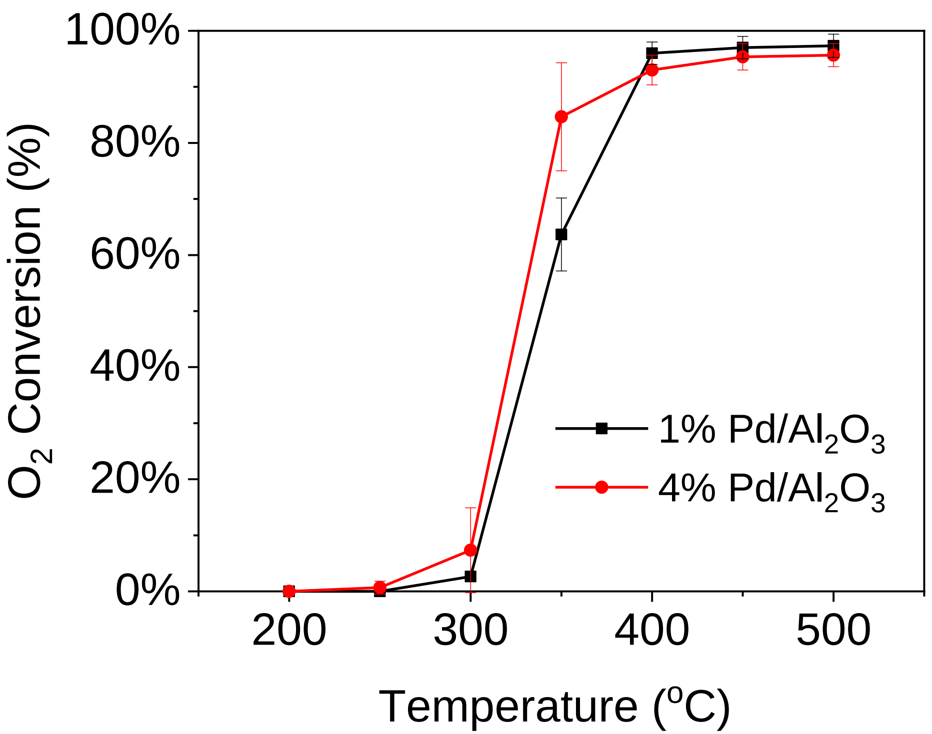
XPS multiplex spectra

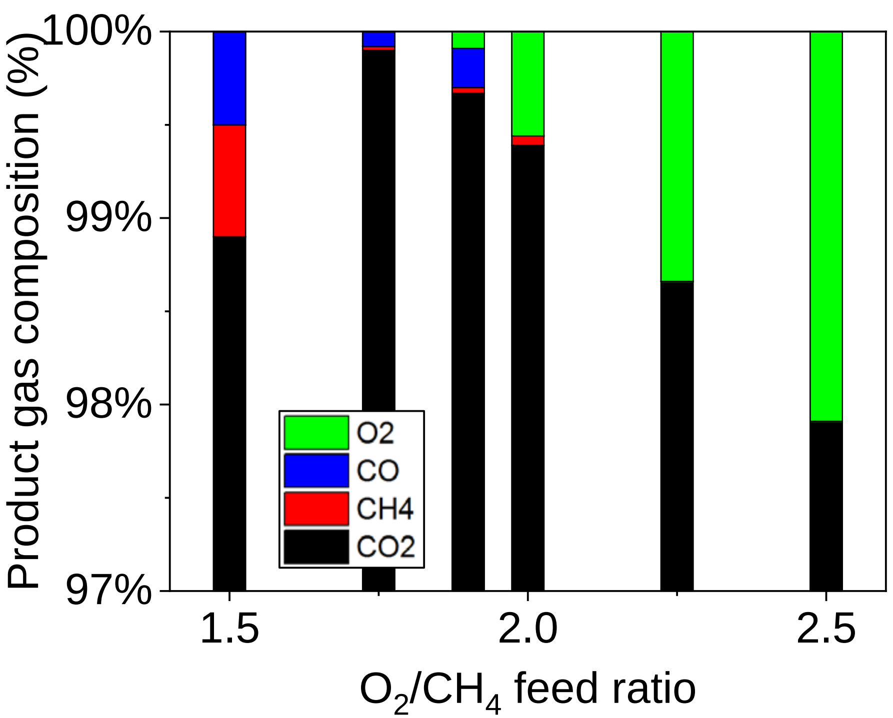
Sample	Pd (%)	PdOx (%)	PdO (%)
5%Pd/TiO_2	45.86	27.49	26.64
3%Pd/TiO_2	61.49	14.73	23.78
1%Pd/TiO_2	29.14	28.98	41.89
5%Pd-5%Ce/TiO_2	36.65	21.30	42.06

Sample	O_α (%)	O_β(%)	O_γ (%)
5%Pd/TiO_2	19.59	44.81	35.60
3%Pd/TiO_2	20.88	57.05	22.07
1%Pd/TiO_2	26.02	53.18	20.80
5%Pd-5%Ce/TiO_2	31.95	47.58	20.46

- ~90% O_2 reduction achieved with Pd catalysts
- Stoichiometric reaction with CH_4 and no CO (<3 ppm) detected
- Metal Pd & adsorbed O_2 (O_α) played key roles

Baseline Catalysts Made with Wet Chemistry Technique: Pd or Pd Composite Metals Supported on Alumina





Stoichiometric feed

Ambient pressure; Feed gas: 10% O_2, 5% CH_4 and balance CO_2; GHSV= 30,000 hr^{-1}

Excess CH_4 *Excess O_2*

1% Pd/Al_2O_3 at 450 °C

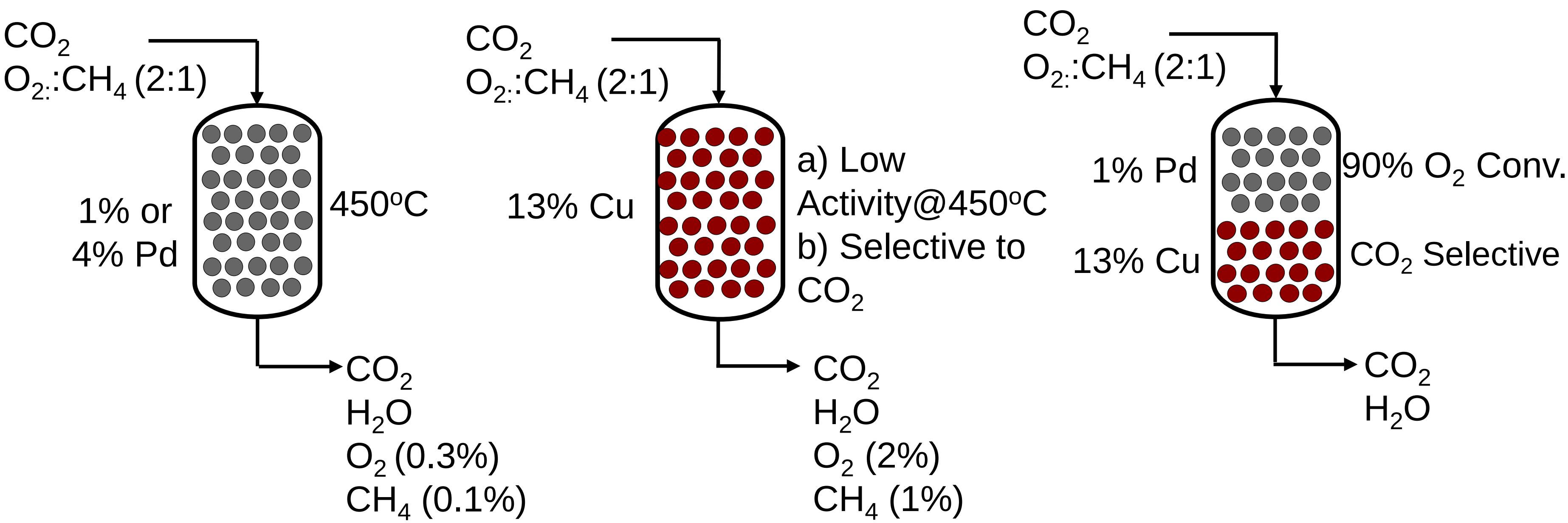
- 1% Pd/Al_2O_3 reduced 97% of O_2 in stoichiometric feed
- 4% Pd/Al_2O_3 earlier light-off; 96% O_2 reduction in stoichiometric feed
- CO formation in excess CH_4 feed (O_2/CH_4 feed ratio <2)

Sequential Pd & Cu Catalysts to Reduce Pd Use and Enhance O_2 Removal and CO_2 Selectivity

Pd/Al_2O_3
Product O_2: ~0.3%

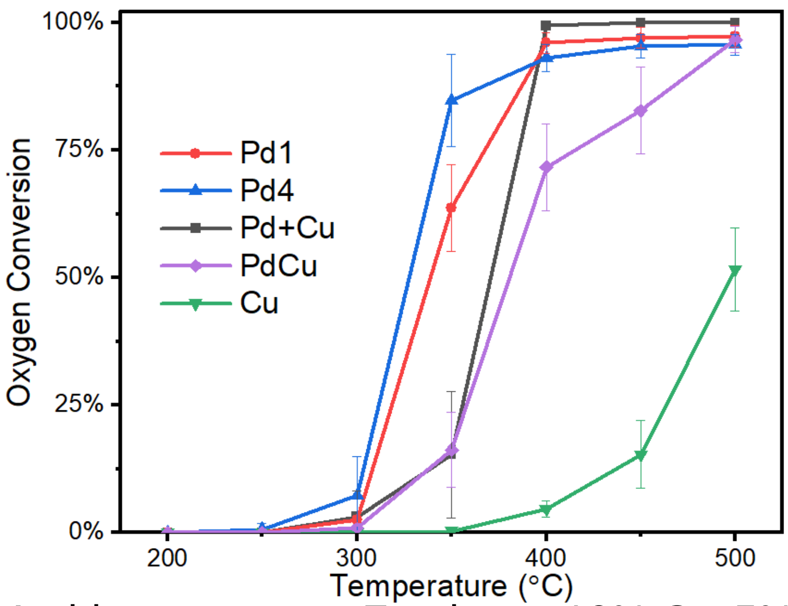
Cu/Al_2O_3
Product O_2: ~2.0%

Pd/Al_2O_3+Cu/Al_2O_3
Product O_2: <500ppm

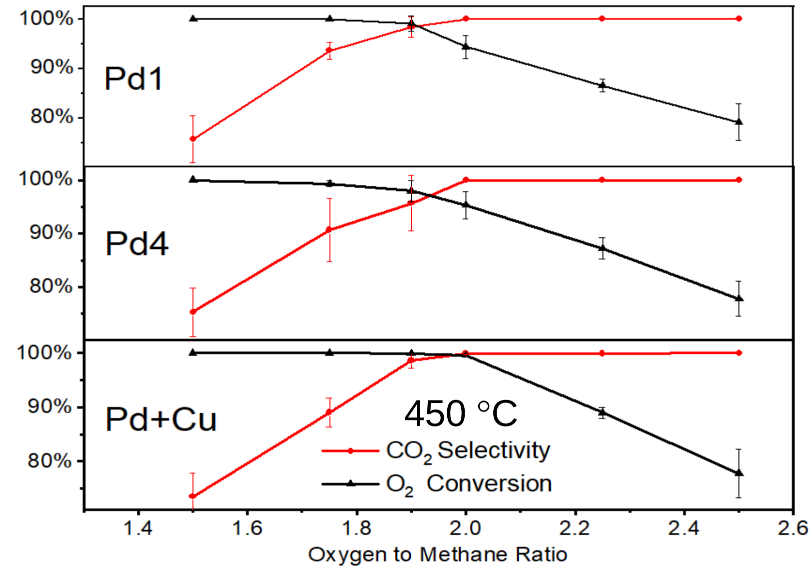


(Pd1: 1% Pd/Al_2O_3; Pd4: 4% Pd/Al_2O_3;
Cu: 13% Cu/Al_2O_3; PdCu: 1% Pd-13% Cu/Al_2O_3;
Pd+Cu: Sequentially layered 4% Pd/Al_2O_3 and 13% Cu/Al_2O_3)

Sequential Pd & Cu Catalysts to Reduce Pd Use and Enhance O_2 Removal and CO_2 Selectivity



Ambient pressure; Feed gas: 10% O_2, 5% CH_4 and balance CO_2. GHSV= 30,000 hr^{-1}



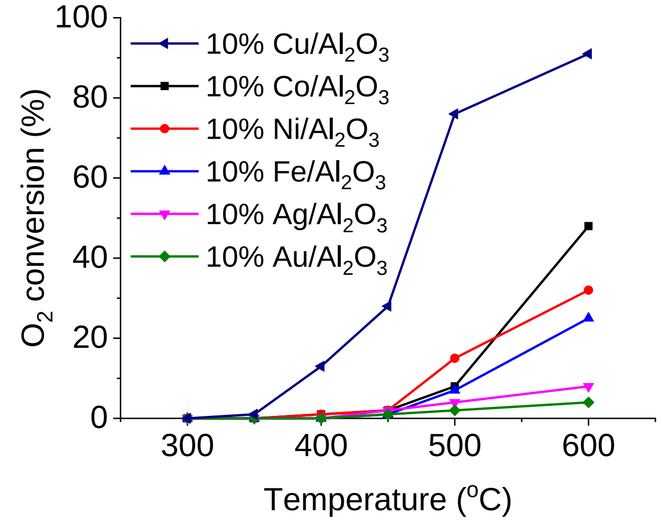
Ambient pressure; Feed gas: 10% O_2, 4.0-6.7% CH_4, balance CO_2. GHSV= 30,000 hr^{-1}

- Pd+Cu had higher O_2 removal than Pd, despite a later light-off T
- Pd+Cu had better activity at near stoichiometry
- Pd+Cu attained both higher selectivity and O_2 removal than Pd

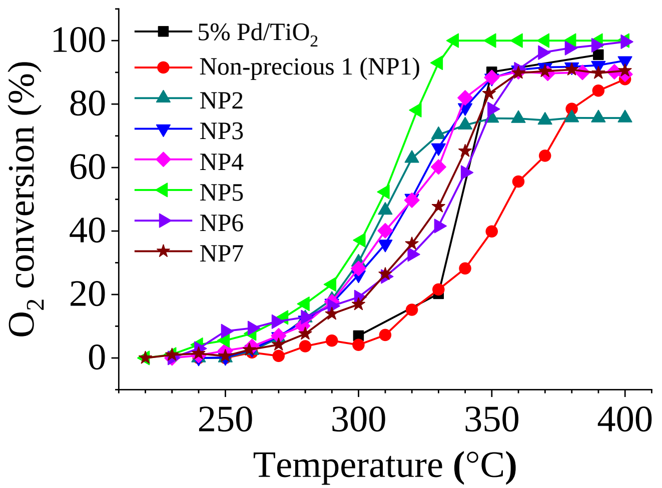
Non-Pd or Non-Precious Metal/Bimetalic Catalysts to Replace Pd and Reduce Material Costs

- Challenges of Pd-based catalysts:
  - High cost
  - Poor CO_2 selectivity in O_2-lean feeds
- Challenges of Cu-based catalysts:
  - Low O_2 reduction activity
  - Degradation due to O_2 adsorption
- Other non-previous catalysts:
  - Low O_2 reduction activity
  - Requires high temperature

Preliminary tests for newly optimized non-previous composite catalysts showed O_2 reduction to <100 ppm without CO formation

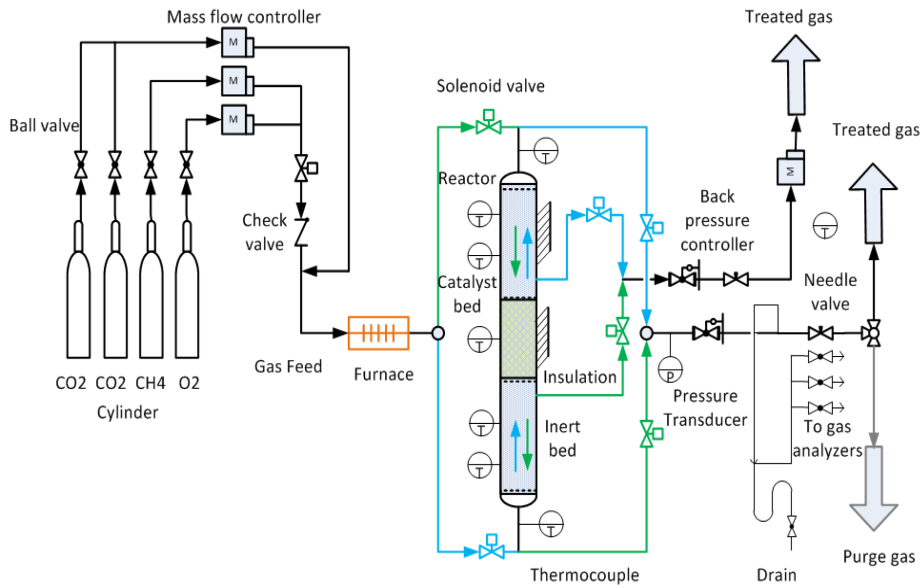


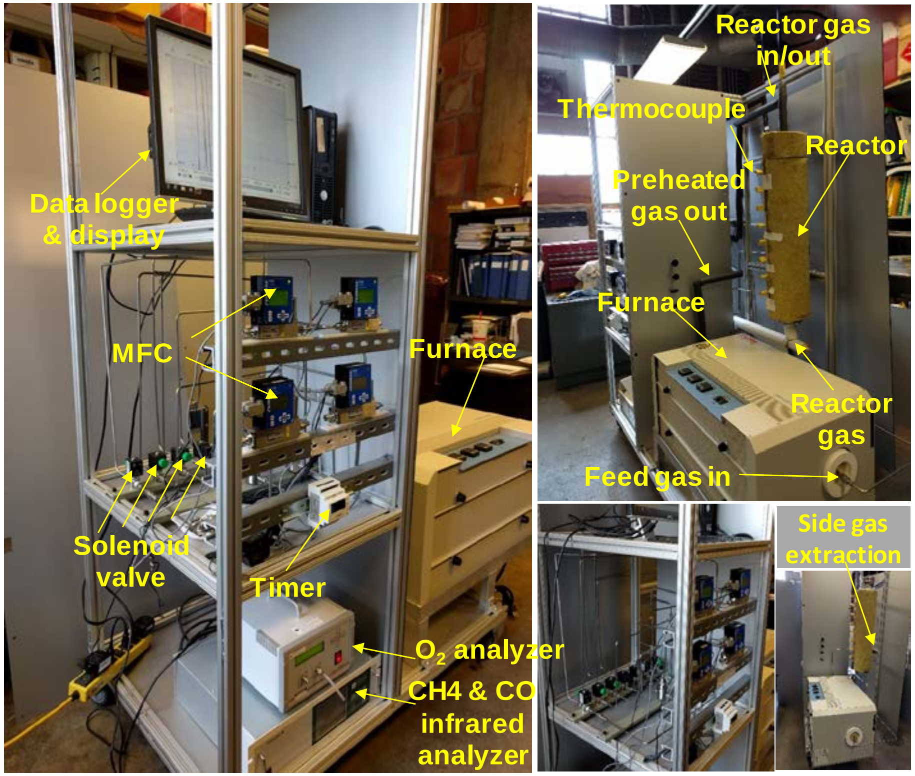
Ambient pressure; Feed gas: 10% O_2, 5% CH_4 and balance CO_2. GHSV= 30,000 hr^{-1}.



Under 15 bar; Feed gas: 3% O_2, 1.5% CH_4 and balance CO_2. GHSV= 30,000 hr^{-1}.

Design and Fabrication of a Bench-Scale High Pressure Reverse Flow Fixed Bed (RFFB) Reactor System

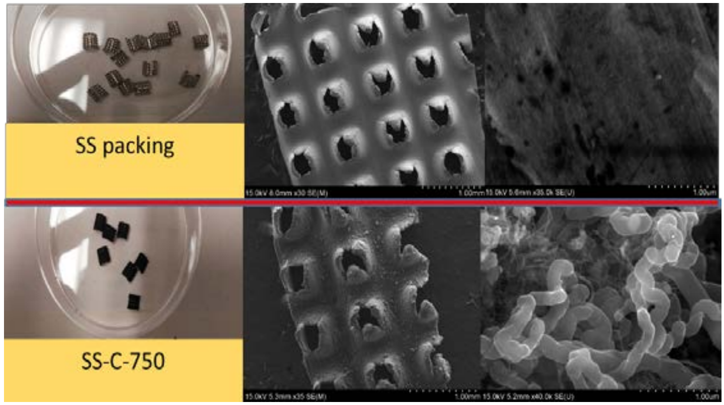




- RFFB system recently built for bench-scale testing of selected catalysts:
  - RFFB reactor of 1” nominal diameter by 28’’ height
  - Rated at 22.5 bar and 750 °C
  - Design flow rate of 15 liter/min (STP)
  - Gas flow direction alternates at a required time interval (e.g., 2 min)
- RFFB design to maintain the required temperature profile for low-concentration reducing gas by storing reaction heat for preheating feed gas

Catalytic Materials for Oxidation and Removal of NO and Hg

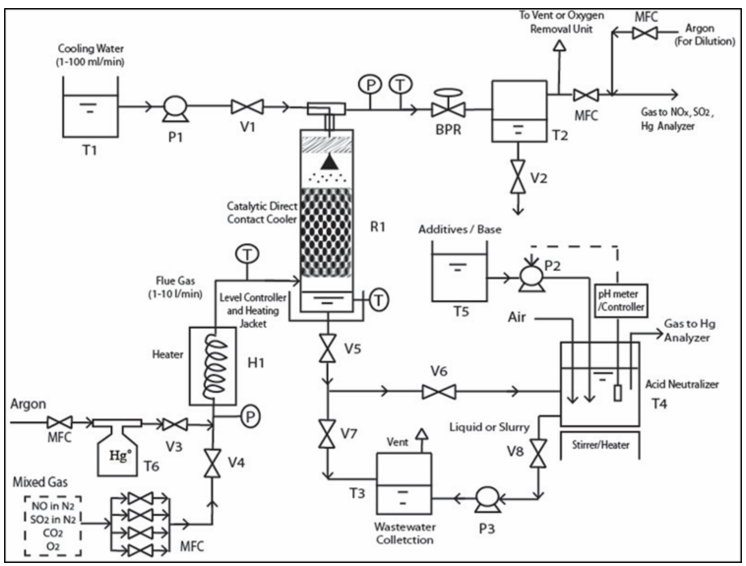
- 3 groups of carbon catalysts were developed:
  - Modified commercially available wood- and coal-based activated carbons (AC);
  - ACs prepared in house from PRB and IL coal;
  - Pyrolytic carbons and carbon nanotubes coated on packing materials
- Preparation or modification methods:
  - Aimed to enhance porosity, develop surface functionalities or catalytic sites, and increase surface hydrophobicity
  - Methods included nitrogen functionalization, Cu or Ce wet impregnation, hydrophobic treatment by silane and acetylene CVD
- >40 catalysts were prepared:
  - Surface area:10-1,677 m^2/g;
  - Water contact angle (WCA) = 0-171º;
  - Porosity: 0.11-0.53 cm^3/g (micro: 22-87%)



Photograph and SEM pictures of as-received and carbon-coated stainless steel packings

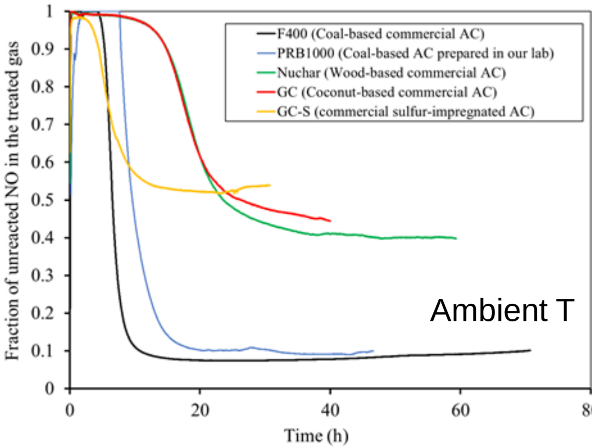
Design and Fabrication of a Bench Scale Catalytic DCC System

- A bench-scale DCC system with replaceable column sizes for testing carbon catalysts (1-100 g) and treating 50-10,000 sccm flue gas
- Bench-scale testing has been initiated

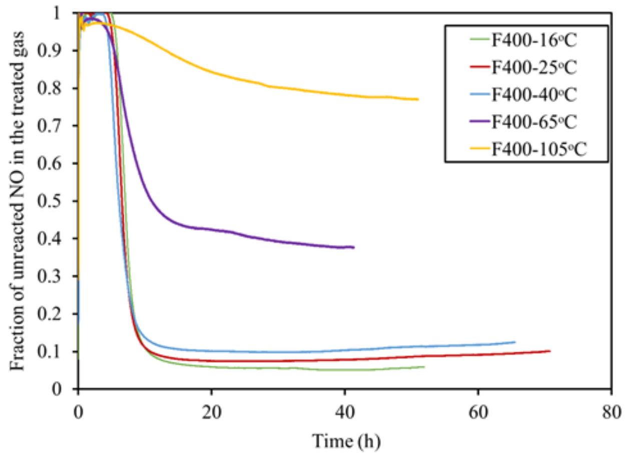


1- Cooling water tank
2- Digital pressure gauge
3- Back pressure regulator
4- Teflon-coated vessel for mercury
5- High pressure cooling water pump
6- Tubular furnace
7- Packed-bed tube reactor
8- Water level controller
9- Mass flow controller
10- Gas-liquid separator
11- Multi channels temperature monitor
12- Peristaltic pump
13- Neutralizer and regent tank
14- pH meter
15- Digital hot plate-stirrer
16- Thermocouples
17- SO_2 analyzer
18- Data logger/computer
19- NO_x analyzer
20- Hg analyzer (to be added later)

Parametric Testing of Catalytic Packing Materials in the Bench-Scale DCC System



Dry mode (w/o water addition)



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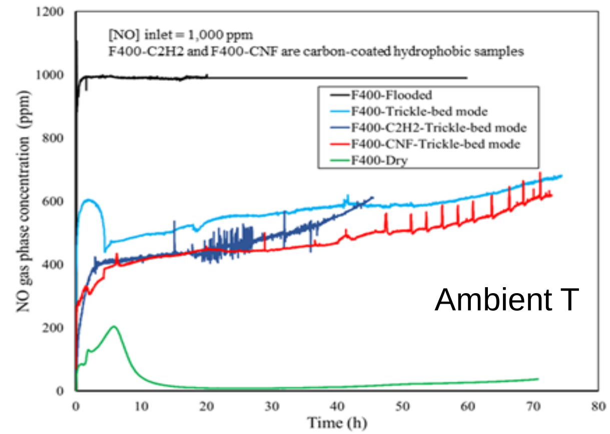


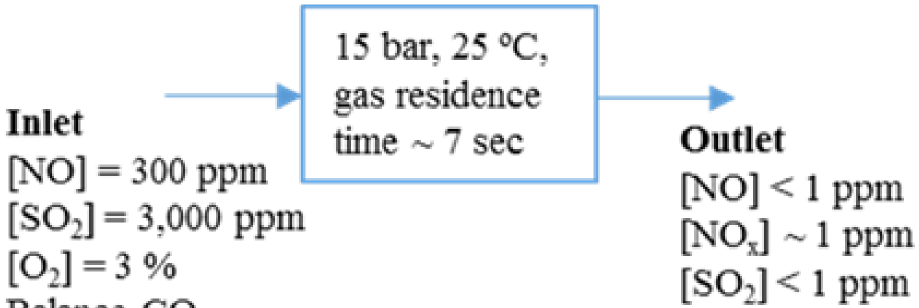
Comparison of dry, flooded, and wet (w/ water addition) mode

Initial catalysts screening was preformed using small-column at atmospheric pressure with feed gas containing 1,000 ppm NO in N_2 and 4% O_2

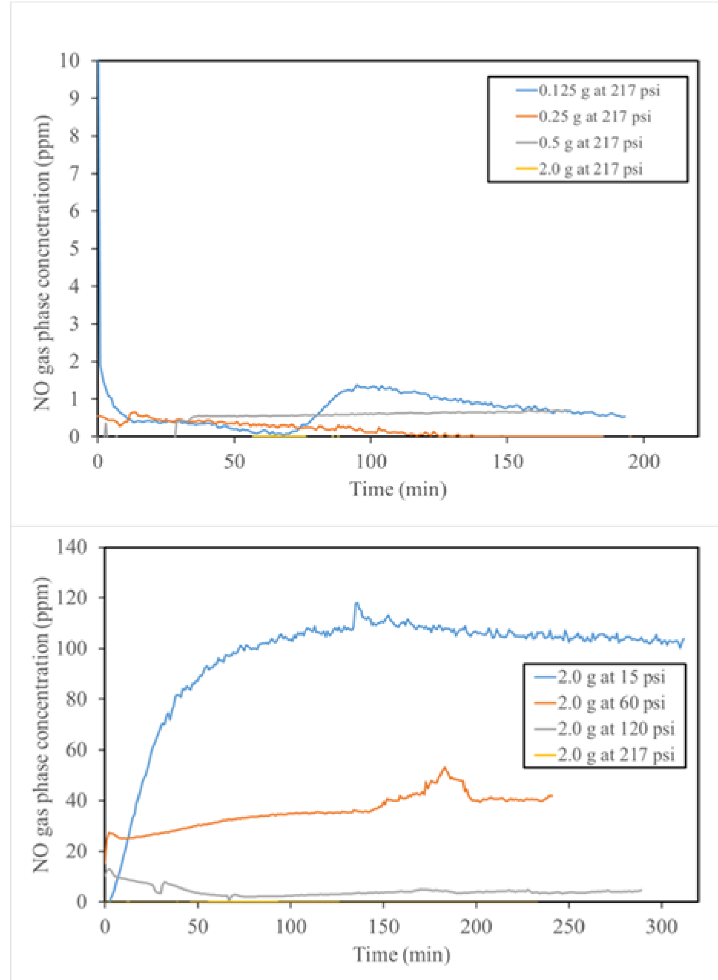
- Generally, coal-based ACs, nitrogen-functionalized, and hydrophobic samples exhibited higher NO conversions
- Higher NO conversion observed at lower temperatures
- Presence of moisture reduced NO conversion
- Catalyst flooding in water resulted in a negligible NO conversion

Parametric testing of catalytic packing materials in the bench scale DCC system

- Small column tests in wet trickle-bed mode performed at different pressures and gas residence times
- NO, SO_2, Hg^0 effectively oxidized on carbon catalysts and removed by wash water
- Increasing pressure significantly enhanced NO oxidation and removal



Hg (100-1000 ppb)

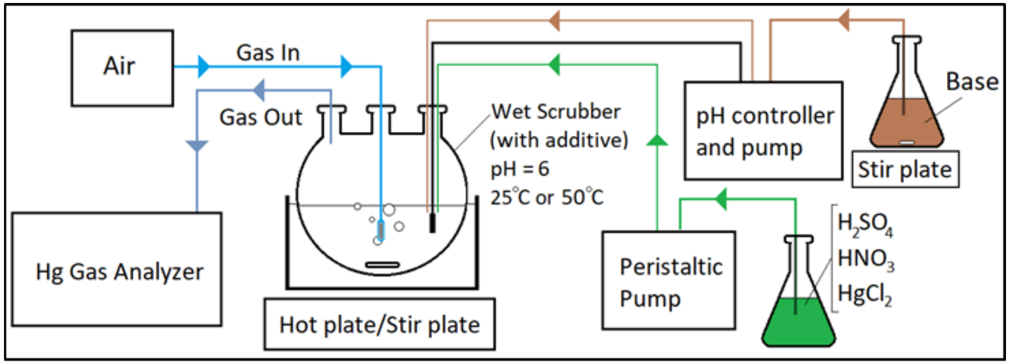


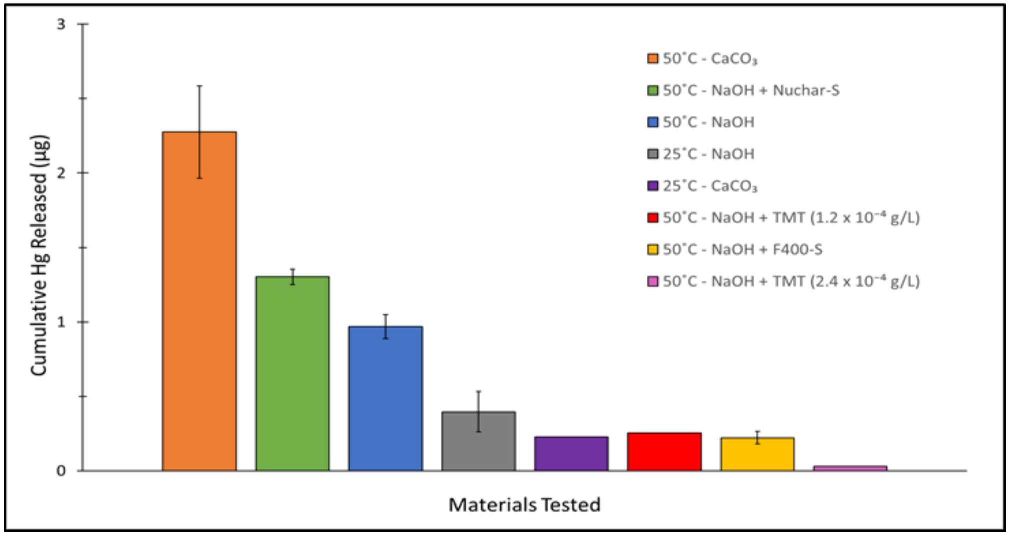
The decision point for achieving >90% removal of NO, SO_2, and Hg from a simulated pressurized flue gas in <10 s successfully passed

Development and Testing of Sorbents Or Additives to Control Hg Reemission from Cooling Water

Experimental method:

- Simulated wastewater contained H_2SO_4, HNO_3 and 0-100 ppb Hg^{2+}
- NaOH solution or $CaCO_3$ slurry as base reagents for neutralization treatment
- Materials tested included S-impregnated ACs (F400-S, Nuchar-S) and the commercially available TMT



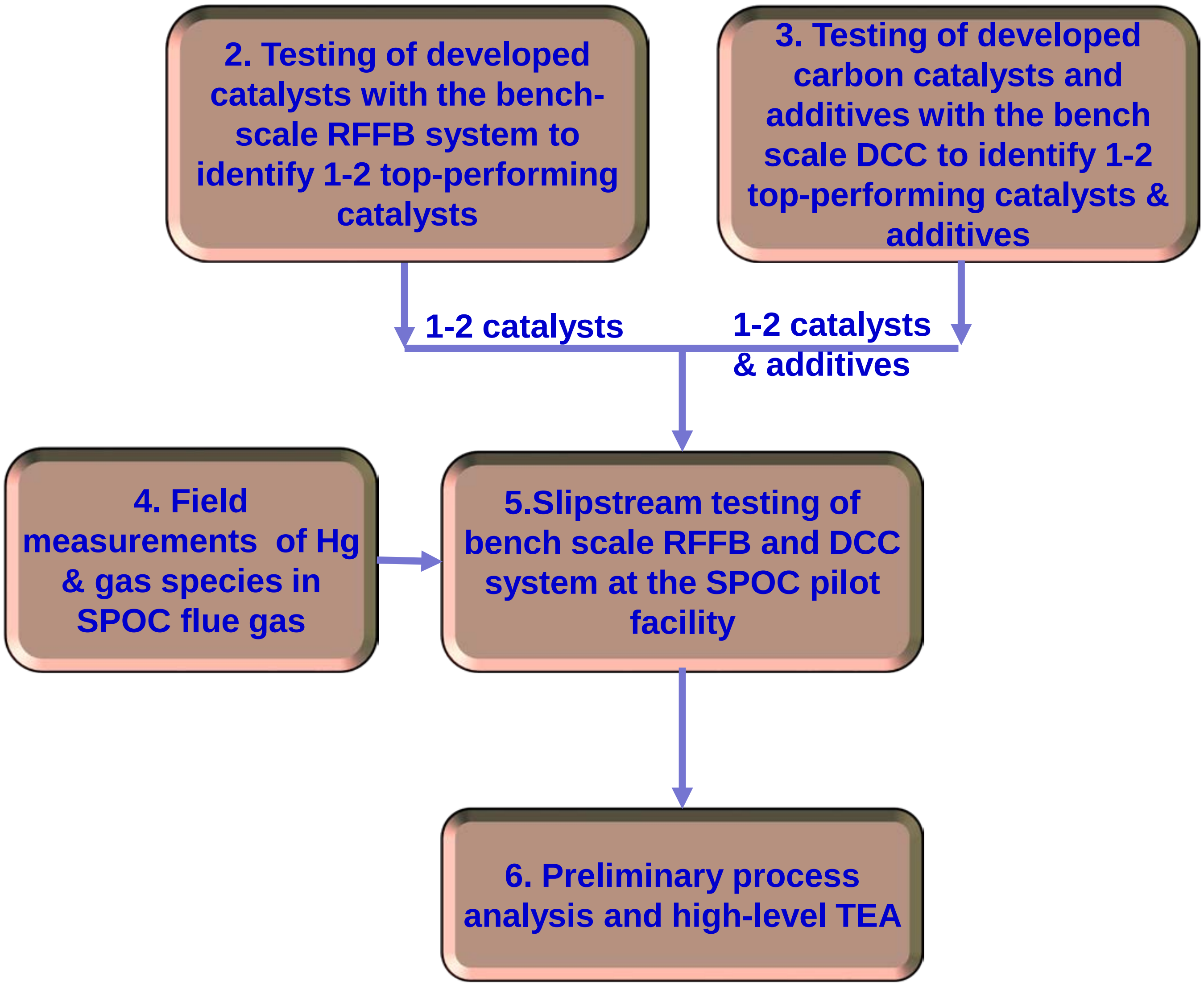


Preliminary results:

- Higher Hg reemission at higher T, indicating wastewater should be cooled prior to neutralization
- Higher Hg reemission with $CaCO_3$ slurry vs. NaOH solution
- Several ACs improved Hg reemission and others did not
- TMT is most effective additive so far

- ❑ Project Overview
- ❑ Technology Background
- ❑ Technical Approach/Project Scope
- ❑ Progress and current status of the Project
- ❑ **Plans for Future Testing, Development or Commercialization**

Plan for Future Work in This Project



Bench scale testing

(50-100 g of sample quantity)

Slipstream testing of bench reactors

(at WUSTL's 100 kW_{th} SPOC pilot facility for about 1 week)

Process analysis & techno-economic analysis (High-level TEA)

Plan for Technology Scale-Up and Commercialization

- Tech development aimed to reach TRL 3 at the end of this project by
  - Validating the proof-of-concept of core technology including catalytic materials and reactor configurations with laboratory development and evaluation;

- Next project aimed to reach TRL 4-5:
  - Catalytic materials are produced at 1-5 kg quantities
  - RFFB and DCC units are integrated and validated in a laboratory or a relevant environment

- Future efforts include engaging engineering groups, utilities, and manufacturers to mitigate engineering and scale-up risks

Comments and Questions?

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