DESIGN OF TRANSITION-METAL/ZEOLITE CATALYST FOR DIRECT CONVERSION OF COAL-DERIVED CO_2 TO AROMATICS

CARBON CAPTURE, UTILIZATION, STORAGE, AND OIL & GAS TECHNOLOGIES INTEGRATED REVIEW MEETING

IMAN NEZAM, GABRIEL S. GUSMÃO, MATTHEW J. REALFF, ANDREW J. MEDFORD, CHRISTOPHER W. JONES

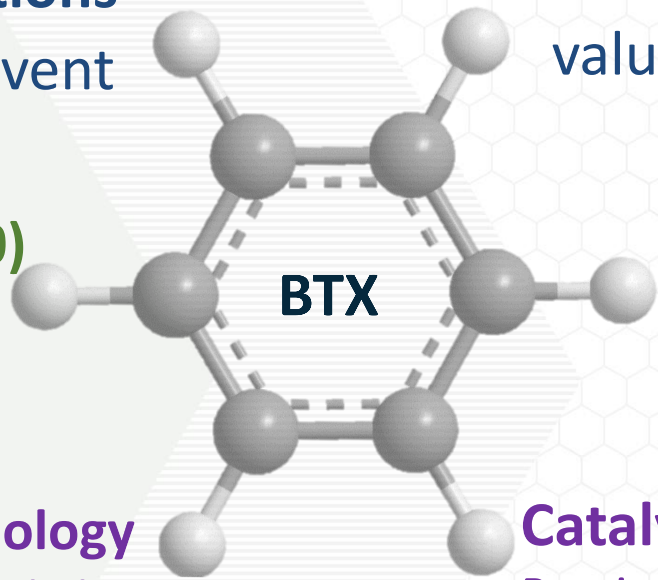
AUGUST 26–30, 2019

CREATING THE NEXT®

Benzene, Toluene, Xylene

Industrial Applications
Solvent

Precursor to
value-added chemicals



Global Production (2010)
100 million metric tons

2050 Projection
200 million metric tons

Current Production Technology
Catalytic reforming of naphtha

Catalyst
Precious metals supported by high surface area materials with acidity

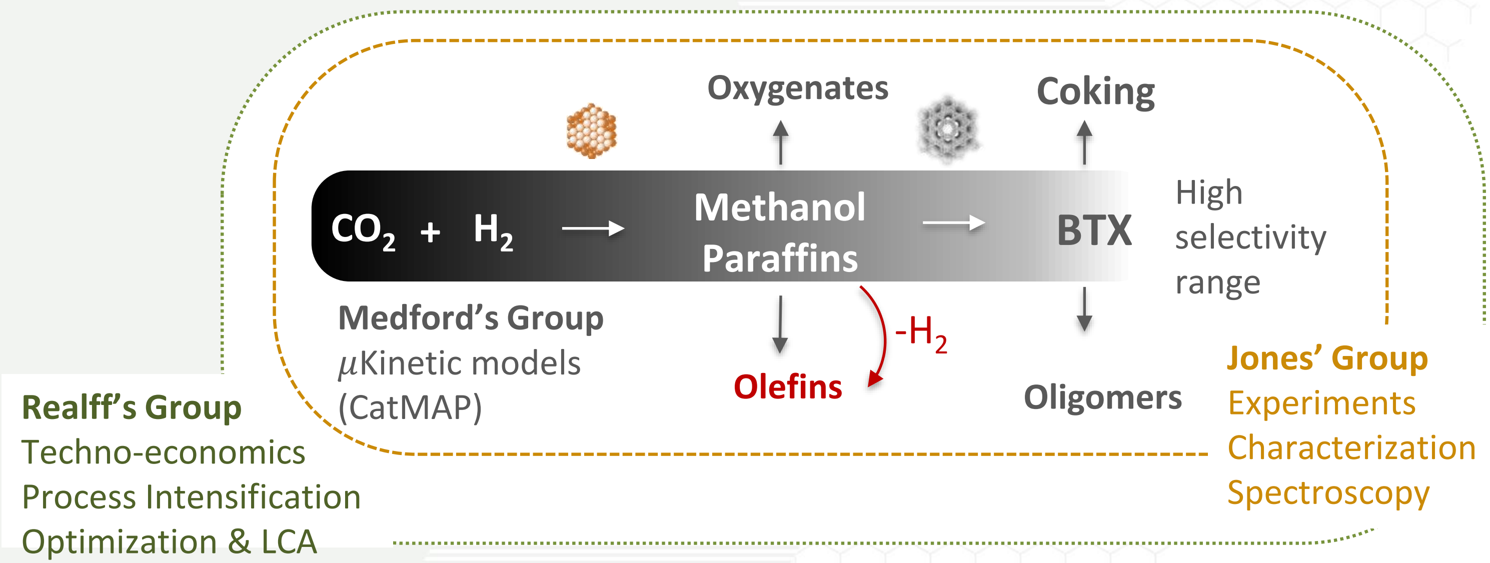
Domestic CO_2 emissions from coal combustion:
~1350 million metric tons in 2016
Could fully support the BTX global market

CO_2 to BTX
(CO_2 → Intermediate → BTX)

Process Intensification approach

Two steps in a single reactor (CO_2 from flue gas, some H_2 source)

1. **CO_2 to Intermediates (Oxygenate / Hydrocarbon):** Trans. Metal (Cu/Co)
2. **Oligomerization + Aromatization:** MFI (ZSM-5)

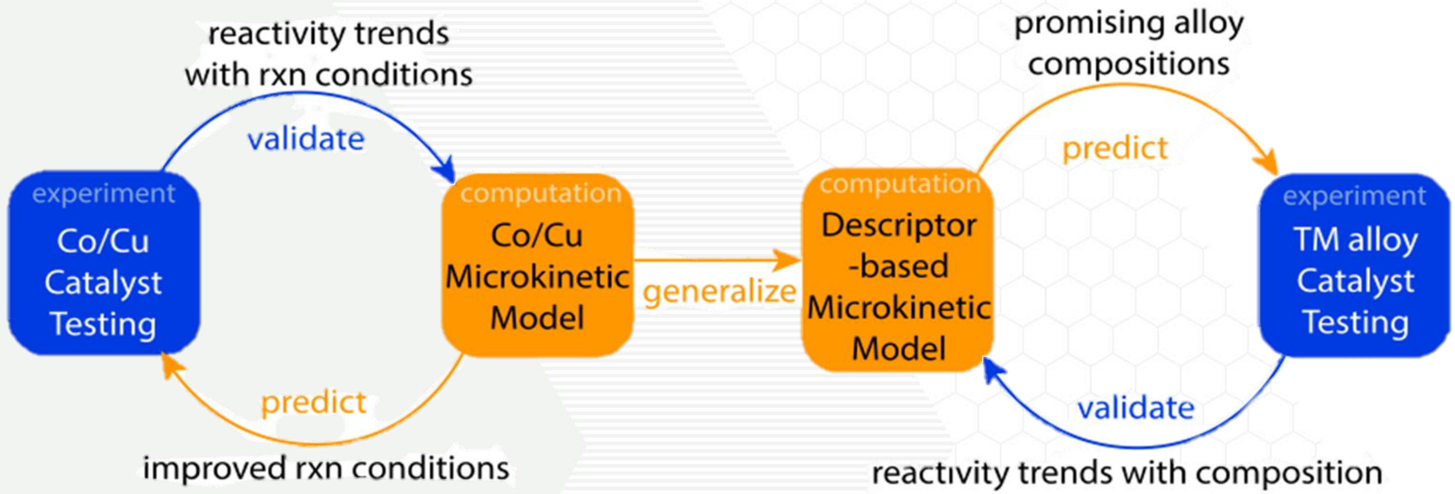


Related Literature Work

Catalyst	WHSV	T	P	H_2/CO_2	X	S	Y	Ref.
Unit	(ml/g/h)	(°C)	(bar)		%	%	%	
$Na–Fe_3O_4$/HZSM-5	4800	320	10	3	29	44	13	Xu et al., Catal Sci Technol, 2019
Fe/HZSM-5	60	350	2	2	38	22	8	Kuei et al., Can J Chem Eng, 1991
ZnZrO/HZSM-5	1200	320	40	3	14	41	6	Li et al., Joule, 2019
ZnO/ZrO_2-ZSM-5	4800	340	30	3	9	50	5	Zhang et al., J CO_2 Util, 2019
$ZnAlO_x$/H-ZSM-5	6000	320	30	3	9	47	4	Ni et al., Nat Commun, 2018
Na-Cu-Fe/H-ZSM-5	3000	250	20	3	12	24	3	Xu et al., J Mol Catal A-Chem, 1998

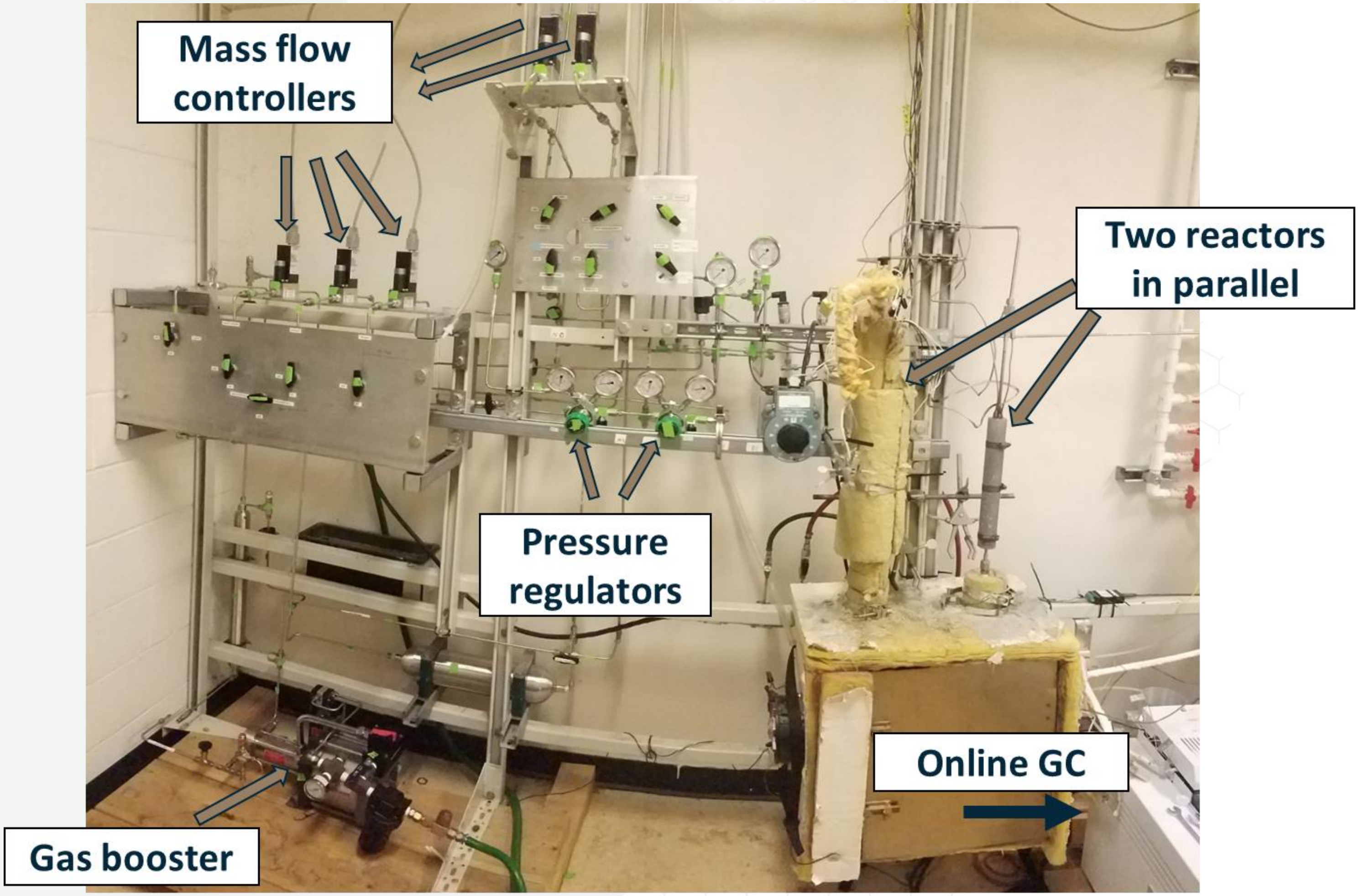
- Limited published studies
- Narrow range of operational conditions/ catalytic characteristics
- No modeling insight available

Experimental Design Strategy



- Retrofitting the reactor
- Computational/experimental investigation of the baseline systems
- Synthesize more complex composite catalyst systems
- Develop reaction/transport models and improve computational model
- Computational model refinement
- Completion of technical and economic feasibility assessments

Experimental Progress



Computational Catalysis Progress

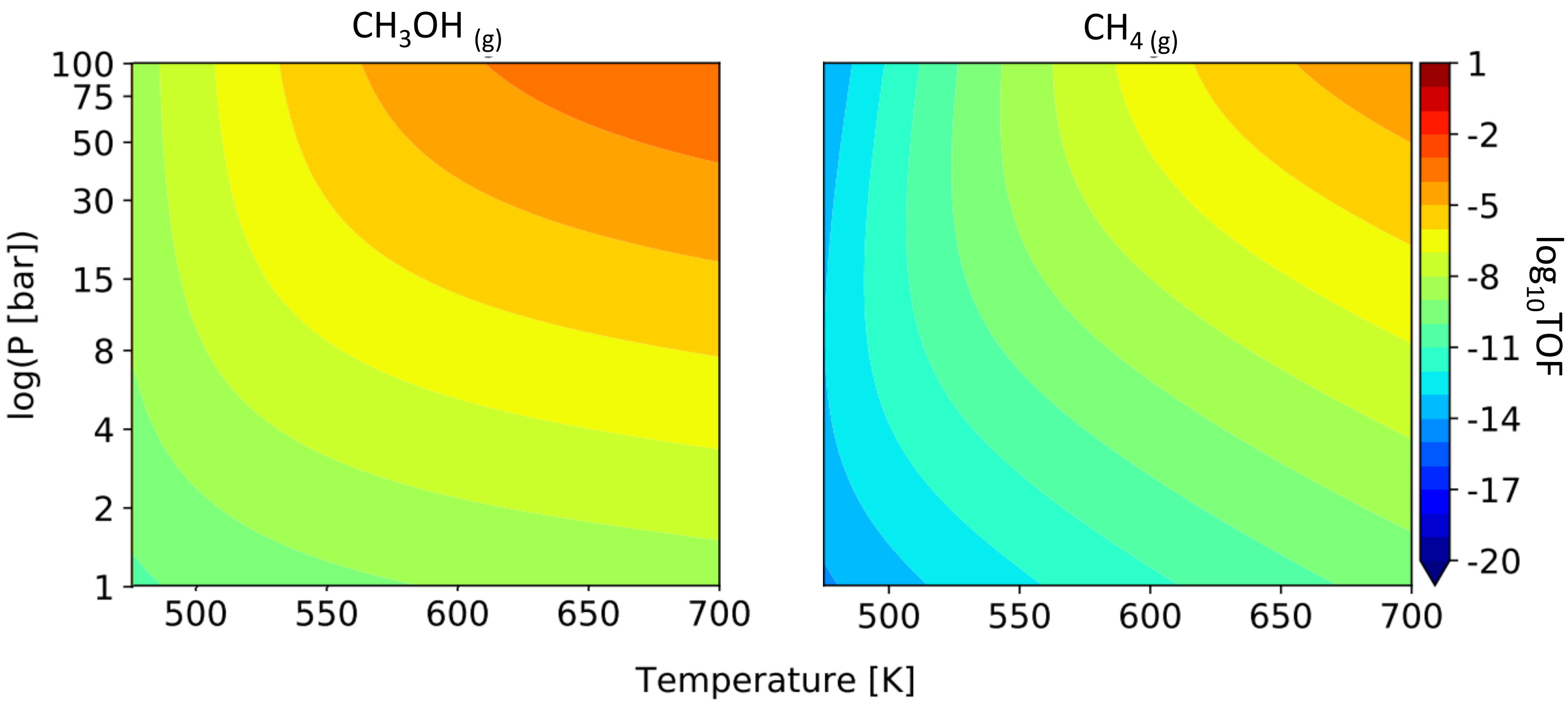
Comprehensive DFT-based mean-field microkinetic catalytic model
28 adsorbate- and 13 gas-species in 42 elementary reactions on Cu(111)

Forward and reverse water-gas shift from [1] *Grabow, L.C. and M. Mavrikakis, ACS Catal., 2011.*
Oxygenates
methanol, formic acid, formaldehyde from [1].
ethanol, acetic acid and acetaldehyde from *Schumann, J. et al., ACS Catal., 2018.*
Hydrocarbons
methane [1] and ethane from *Martin Hangaard, H. et al., J. Catal. 2019.*
Oxygen dissociation from *Falsig, H., et al., Top. Catal., 2014*

Computational Catalysis Progress

DFT-based Catalytic Activity for main CO_2 reduction products

at gas phase concentration 0.90:0.05:0.05 H_2:CO_2:CO



CREATING THE NEXT®

Conclusions

- An experimental process rig has been developed for the catalytic conversion of CO_2 to aromatics.
- DFT-based rates have been calculated for the main expected intermediate species for the CO_2 hydrogenation on Cu(111).

Next steps

- Performing experimental analysis using baseline and tandem catalysts.
- Carry out DFT-calculations for the same microkinetic model on Co(211).

Acknowledgements

We acknowledge the U.S. Department of Energy for financial support through grant DE-FE0026433.

Thank You!