Modular Production of Olefins from Natural Gas

Congjun Wang, Sittichai Natesakhawat, Christopher Matranga, Jose Lopez, Setrak Tanielyan, Daniel Guerrero, Raghubir Gupta

FWP-1022467

2021 Carbon Management and Oil and Gas Research Project Review Meeting, August 2021

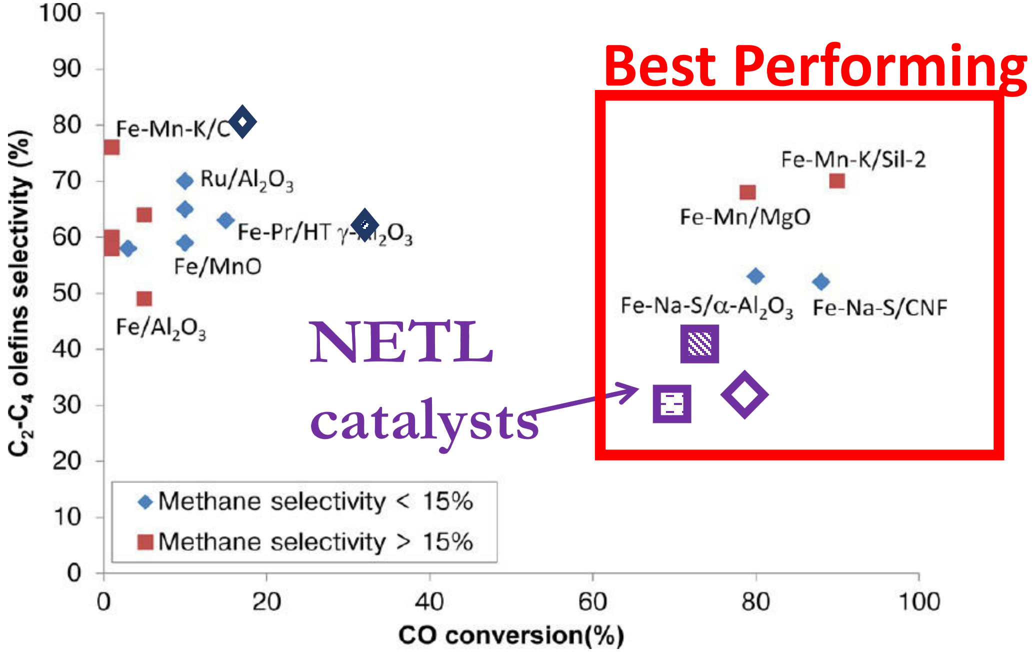
NATIONAL ENERGY TECHNOLOGY LABORATORY
SETON HALL UNIVERSITY
Susteon

Presentation Outline

NATIONAL ENERGY TECHNOLOGY LABORATORY

- **Project Overview**
- Technical Progress
  - Natural gas to syngas w/plasma reactor
  - Syngas to olefins w/nanostructured Fe/C catalysts
    - Synthesis, Optimization, and Characterization of Catalysts
    - Performance Testing of catalyst for syngas to olefins synthesis
  - Modular natural gas to olefins process modeling and preliminary TEA
- Conclusion and Future Work

Previous Work & Motivation



Adapted from: H. M. Torres Galvis, K. P. de Jong, *ACS Catal.* 3, 2130−2149 (2013).

- **2016-2019: Nanostructured Fe on Carbon low temp syngas to olefins catalyst developed**
- **NETL catalyst among best performing in literature**
  - High CO conversions
  - Good C2-C4 olefin selectivity
  - Long lifetimes (300+ hours)
- **Low temp olefins production from natural gas helps environment**
  - Alternative to natural gas flaring/venting
  - Alternative to high temp catalytic cracking used w/petroleum feedstocks

Project Overview

Project Objectives:

- Integrate patent-pending NETL catalyst into a modular natural gas to olefins process
- Characterize performance and cost of modular process using experiments and paper-based process modeling
- Conduct preliminary TEA to evaluate commercial potential.

ChemCatChem **11**, 1625-1632 (2019).
International Patent Application filed 01/2020, publication number WO 2020/150129 A1.

Project Approach

- **Establish Industry Collaboration to Guide Research & Tech Transfer**
  - Cooperative Research and Development Agreement (CRADA) est. w/Susteon
  - Formal agreement signed Dec 2020
- **Integrate Catalyst into a Modular Natural Gas to Olefins Process**

  1) Convert Natural Gas to Syngas w/Catalytic Plasma Reactor
  - Proprietary technology, owned by Susteon LLC, provided at **NO COST** to project
  - Process conditions modified to produce 0.7-1 ratio of H_2/CO syngas
  - Provides mass/energy data for process development/modeling

  2) Convert Syngas to Olefins with Nanostructured Fe/C Catalyst
  - Developed by NETL 2016-2019
  - One of the best performing FTO catalyst reported in literature
  - Reaction studies provide mass/energy balance for FTO process development/modeling

  3) Develop Paper-based Process Model as Initial Estimate of Performance/Costs
  - Aspen or other package to model full NG to Olefins process
  - Gas cleanup/separations, other units, will be "off the shelf" from modeling software
  - Goal is to create non-granular, process model to capture important details/costs, & direct future work

Project Timeline

3 Technologies Evaluated:

- **Non-thermal Catalytic Plasma Reactor:** Natural Gas to Syngas Production
- **Nanostructured Fe Catalysts:** Syngas to Olefins Production
- **Integrated Modular Natural Gas to Olefins Process:** Paper-based Process Modeling & Preliminary TEA

Approximate Project Timeline

- **Year 1:** Catalyst and Plasma Reactor Evaluation/Shakedown, Initial Process Development/Evaluation
  - Evaluate Fe/C catalyst at realistic industrial conditions
  - Evaluate plasma reactor at wet/dry reforming conditions to produce 0.7-1 ratio of H_2/CO
  - Utilize mass/energy balance data for process modeling & preliminary TEA
  - **Go/No Go Decision 10/1/2021**
- **Year 2:** Materials and System Scale Up
  - Hire specialized external vendor to make catalyst in 50 Kg batches
  - Evaluate performance at bench scale w/comparison to previous results
  - Refine process model and TEA
- **Year 3:** Pre-pilot Testing and Evaluation
  - Evaluate 50 Kg batches in appropriate pre-pilot scale system
  - Further refine process model/TEA
  - Utilize TEA to estimate commercial potential of modular natural gas to olefins process at scale

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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Natural Gas to Syngas w/Plasma Reactor System

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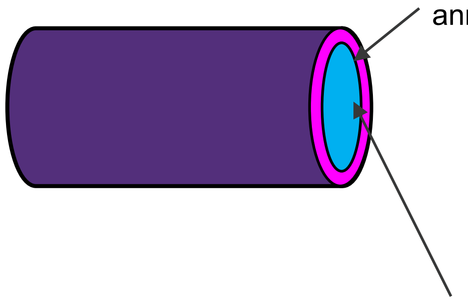
Dry Methane Reformation

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$$



Dry Methane Reforming Summary

Operational Parameters						Efficiency parameters		
CO_2/CH_4	Temp	CH_4 Res Time	Plasma Voltage		CH_4 Conversion, %	CO_2 Conversion, %	H_2 Selectivity, %	CO Selectivity, %
Mol/mol	°C	s	V					
4.0	200	6	No plasma		3.3	10.8	1.8	8.6
			15,000		13.4	8.0	36.2	66.8
			17,000		40.5	20.8	40.7	50.2

Reference Data Files (Year 2021):

Table 1. NETL_Apr_20
Table 2. NETL_Apr_28
Table 3. NETL_July_07

Catalytic Non-Thermal Plasma (CNTP) reactor developed in collaboration with Susteon

Susteon

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Syngas to Olefins w/Nanostructured Fe/C

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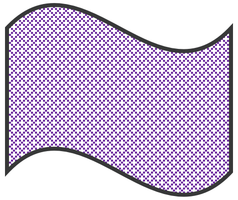
Two-step synthesis of carbon support and iron oxide catalysts

Carbon Support

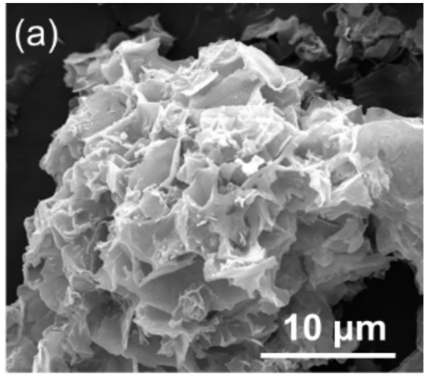
$(HOC(COOK)(CH_2COOK)_2 \cdot H_2O$
potassium citrate

850 °C, 1 hr → N_2

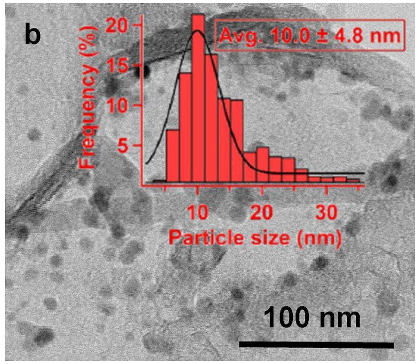


carbon nanosheets (catalyst support)

"Rose Petal" Structure

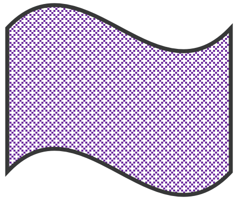


~10 nm Fe particles



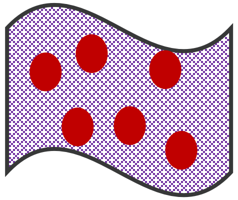
Fe on Carbon Support

$(NH_4)_5Fe(C_6H_4O_7)_2$ +
ammonium iron citrate



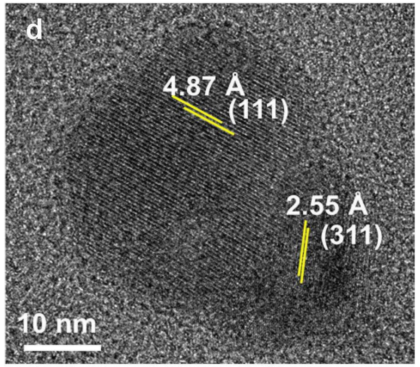
carbon support

500 °C, 2 hr → N_2

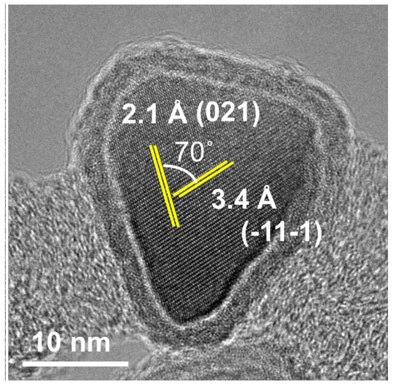


Fe_xO_y on carbon support

Fe Before Rxn



Fe After Rxn

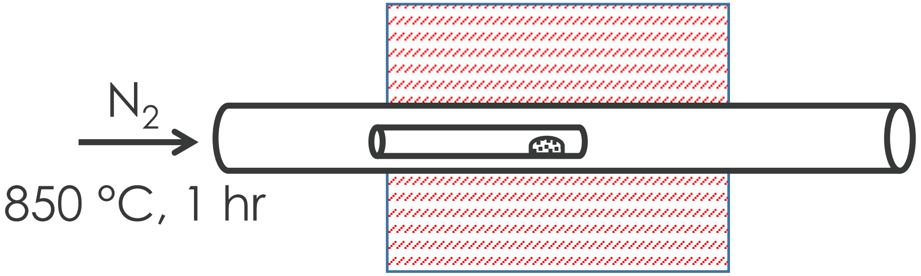


Synthesis details: Zhou et. al. ChemCatChem 2019, 11, 1625–1632

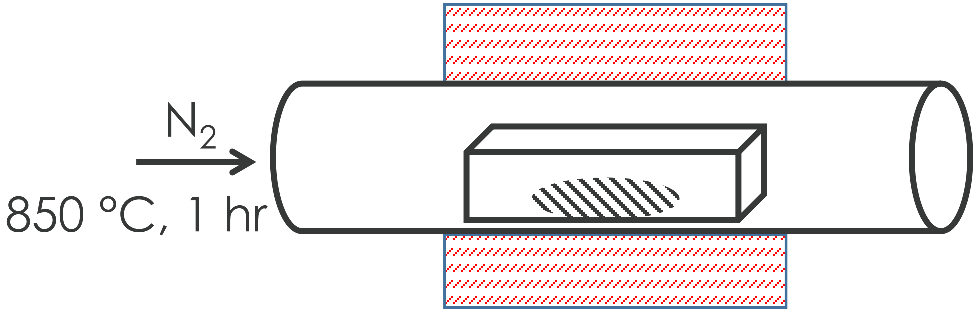
Syngas to Olefins w/Nanostructured Fe/C

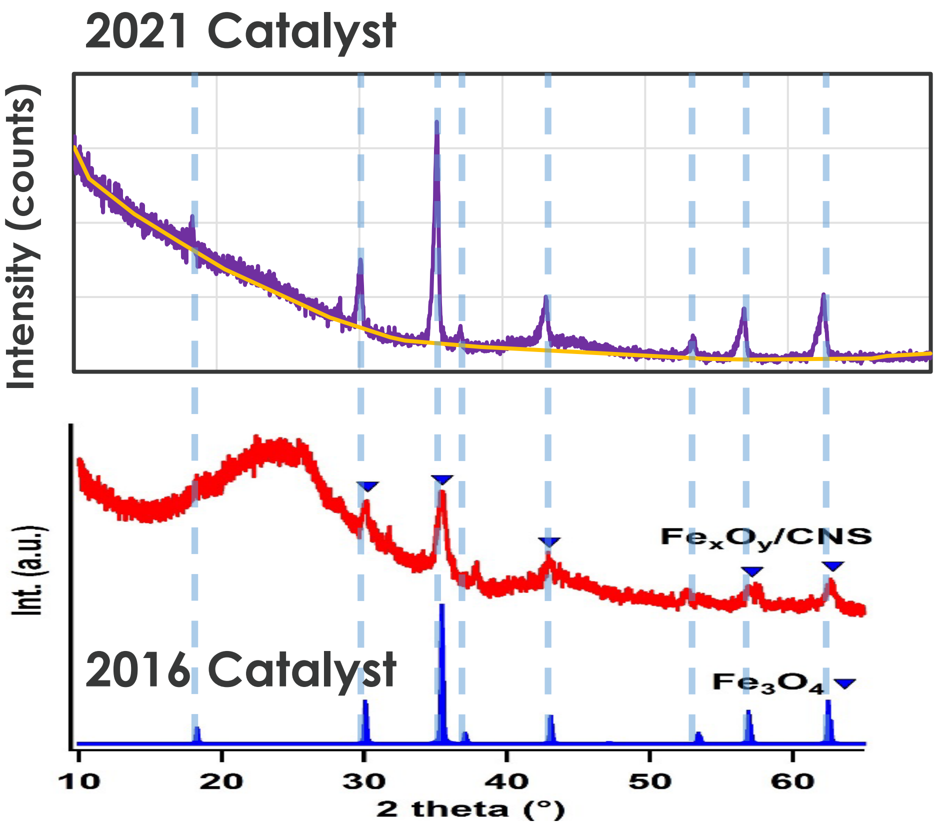
- Previous synthesis method from 2016 too small of scale for current project needs
- Switched to larger crucible used to make sufficient sized batches for internal/external testing in 2020/2021
- This caused unexpected and significant changes to catalyst material that caused **unexpected project challenges**

2016: 10s of milligrams per batch (small crucible)



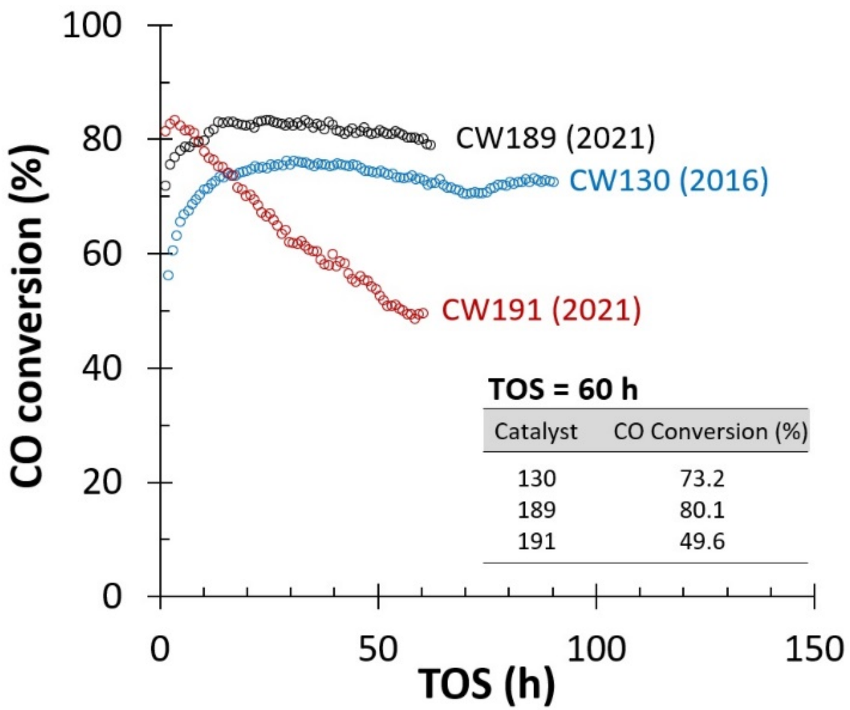
2021: multi-grams per batch (large crucible)



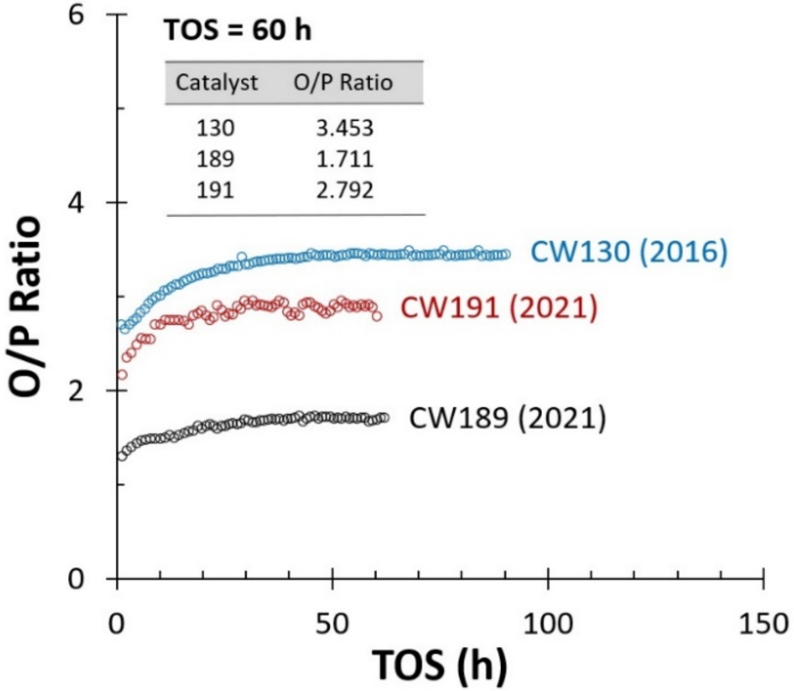


XRD

Syngas to Olefins w/Nanostructured Fe/C



Catalyst	CO Conversion (%)
130	73.2
189	80.1
191	49.6



Catalyst	O/P Ratio
130	3.453
189	1.711
191	2.792

- **2021 Studies found immediate issues w/performance:**
  - **Reactivity was lower or samples deactivated w/time**
  - **More paraffins produced than in 2016 work**
  - **Sample density was lower than in 2016 work**
- ***These issues not observed in 2016 studies***
- ***Changes are likely result of new synthesis scale up***

Syngas to Olefins w/Nanostructured Fe/C

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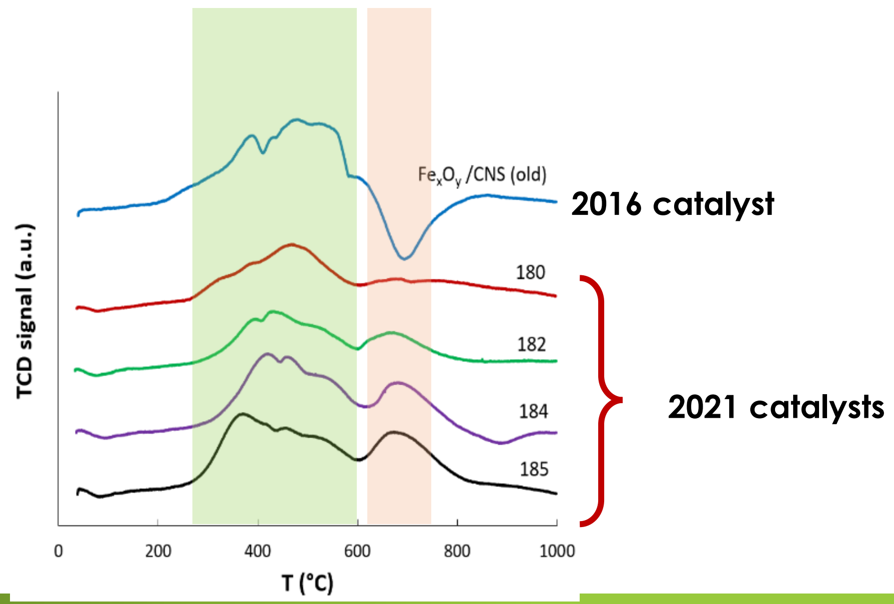
Major Sample Issues Were Identified:

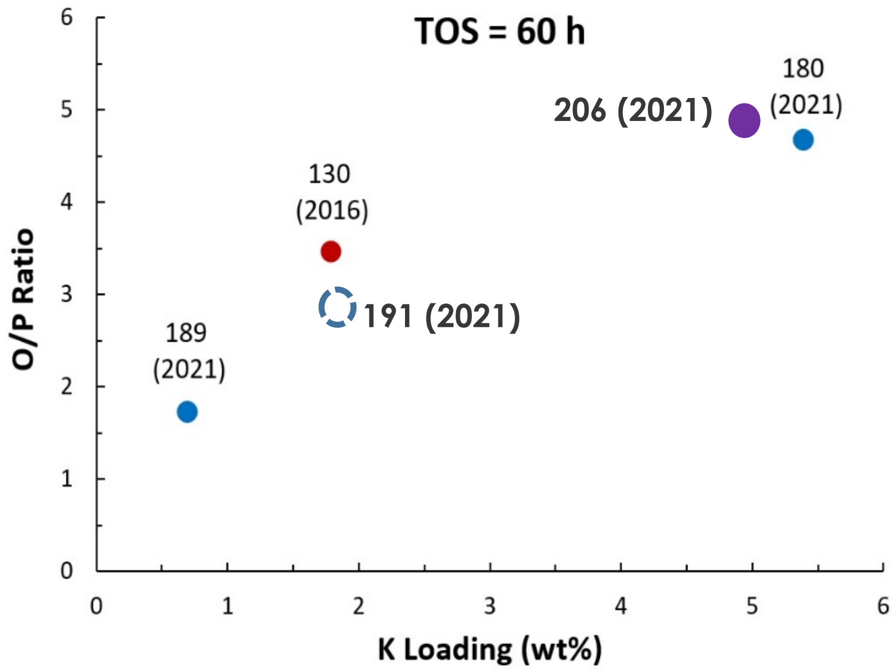
- K levels were varying, unexpectedly
- Surface areas of carbon support 10X larger
- TPR illustrates other reactivity differences

Identified a rinsing step during synthesis as being major issue for this.

Temperature Programmed Reduction



Impact of K-level on Selectivity



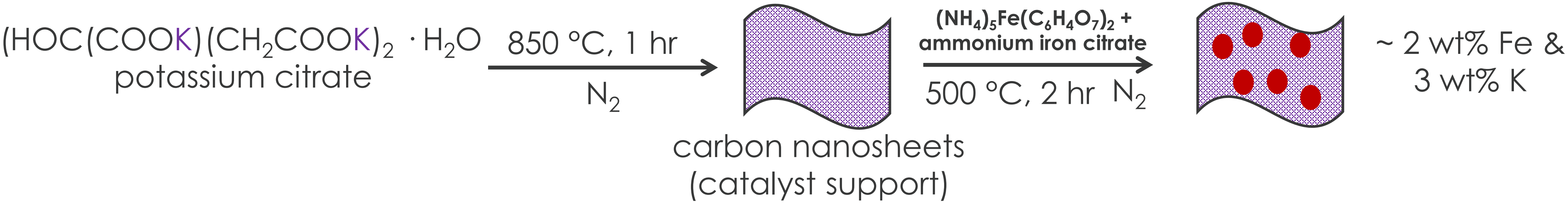
Surface area of 2016 (130) catalyst: 81 m^2/g
Surface area of 2021 catalysts: ~1,000 m^2/g

Syngas to Olefins w/Nanostructured Fe/C

2 Approaches Chosen to Address Sample Issues

#1) 2021: New rinsing & K loading method developed (needs additional optimization)

#2) Return to 2016 method of small batch synthesis & accumulate large batch for testing (first rxn testing scheduled week of 8/16/2021)

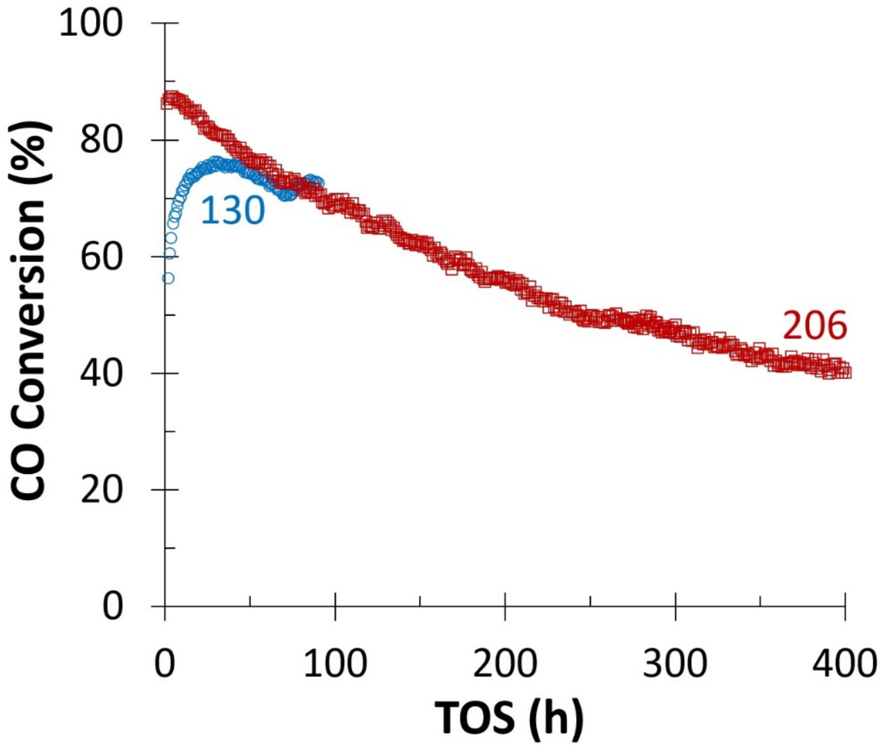


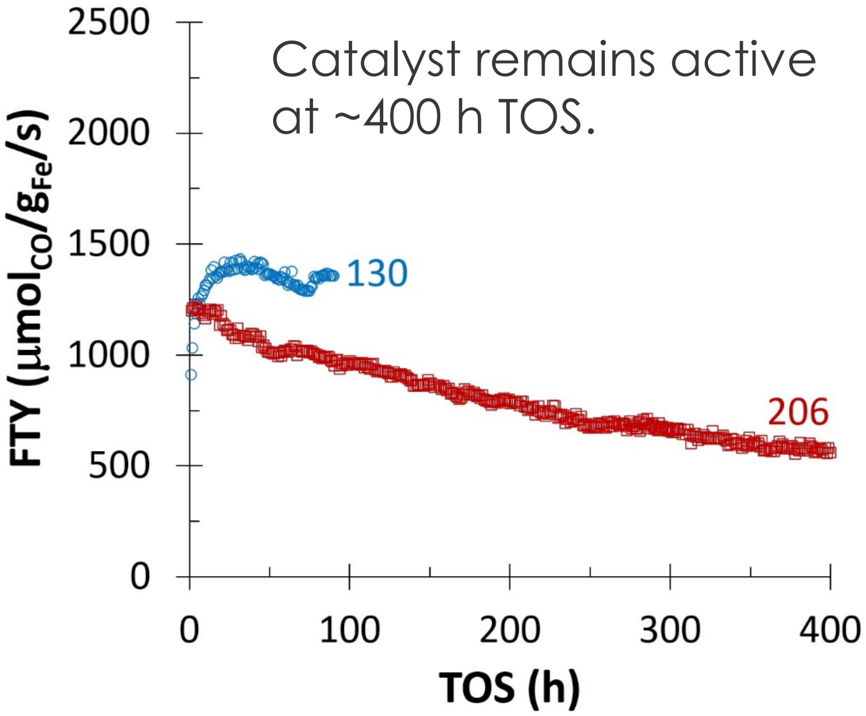
Syngas to Olefins w/Nanostructured Fe/C

Activity & stability

Pretreatment:
400 °C, 1 bar, H_2, 50 sccm, 3 h
Reaction:
350 °C, 20 bar, F_{tot} = 100 sccm, WHSV = 30,000 $cc/g_{cat}/h$

Catalyst	Feed $CO/H_2/N_2$	H_2/CO	TOS (h)	CO conversion (%)	FTY ($\mu mol_{CO}/g_{Fe}/s$)
130	45/45/10	1	90	73	1355
206	30/60/10	2	400	40	560





Catalyst remains active at ~400 h TOS.

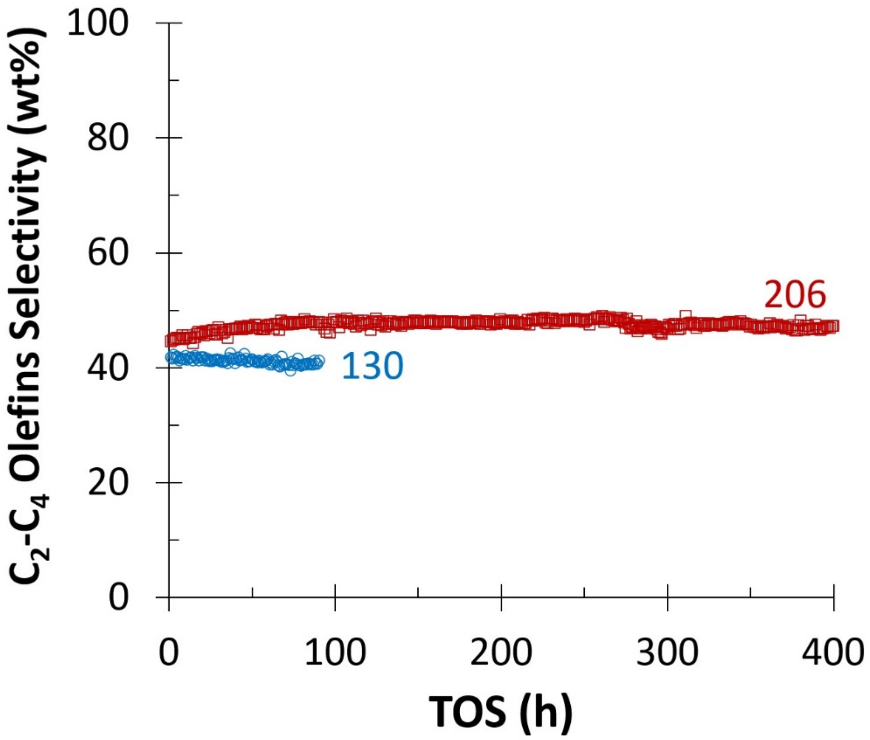
Syngas to Olefins w/Nanostructured Fe/C

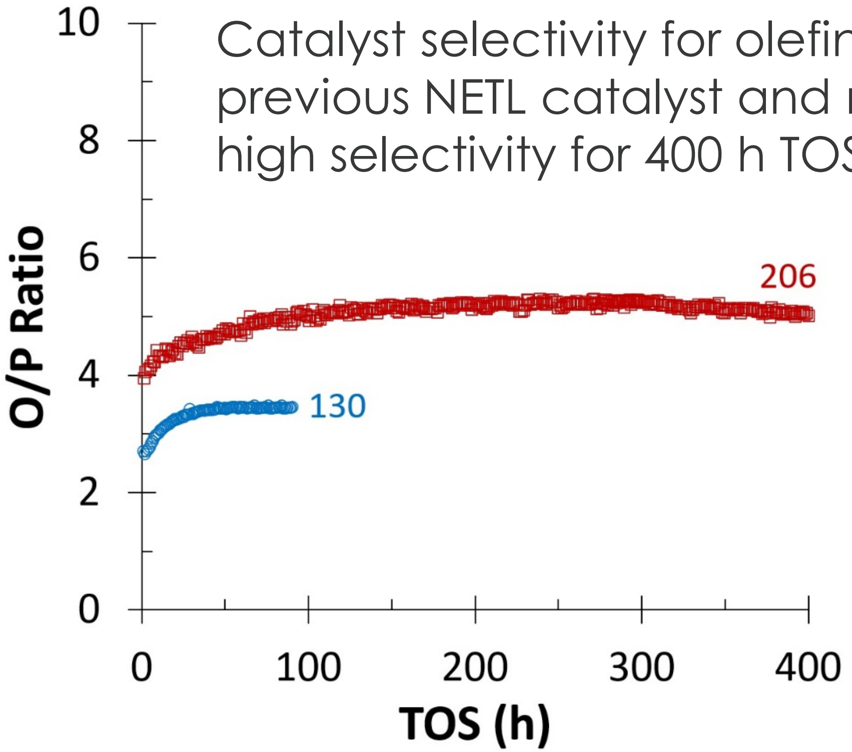
HC product selectivity

Pretreatment: 400 °C, 1 bar, H_2, 50 sccm, 3 h

Reaction: 350 °C, 20 bar, F_{tot} = 100 sccm, WHSV = 30,000 cc/g_{cat}/h

For H_2/CO = 1, $CO/H_2/N_2$ = 45/45/10; For H_2/CO = 2, $CO/H_2/N_2$ = 30/60/10

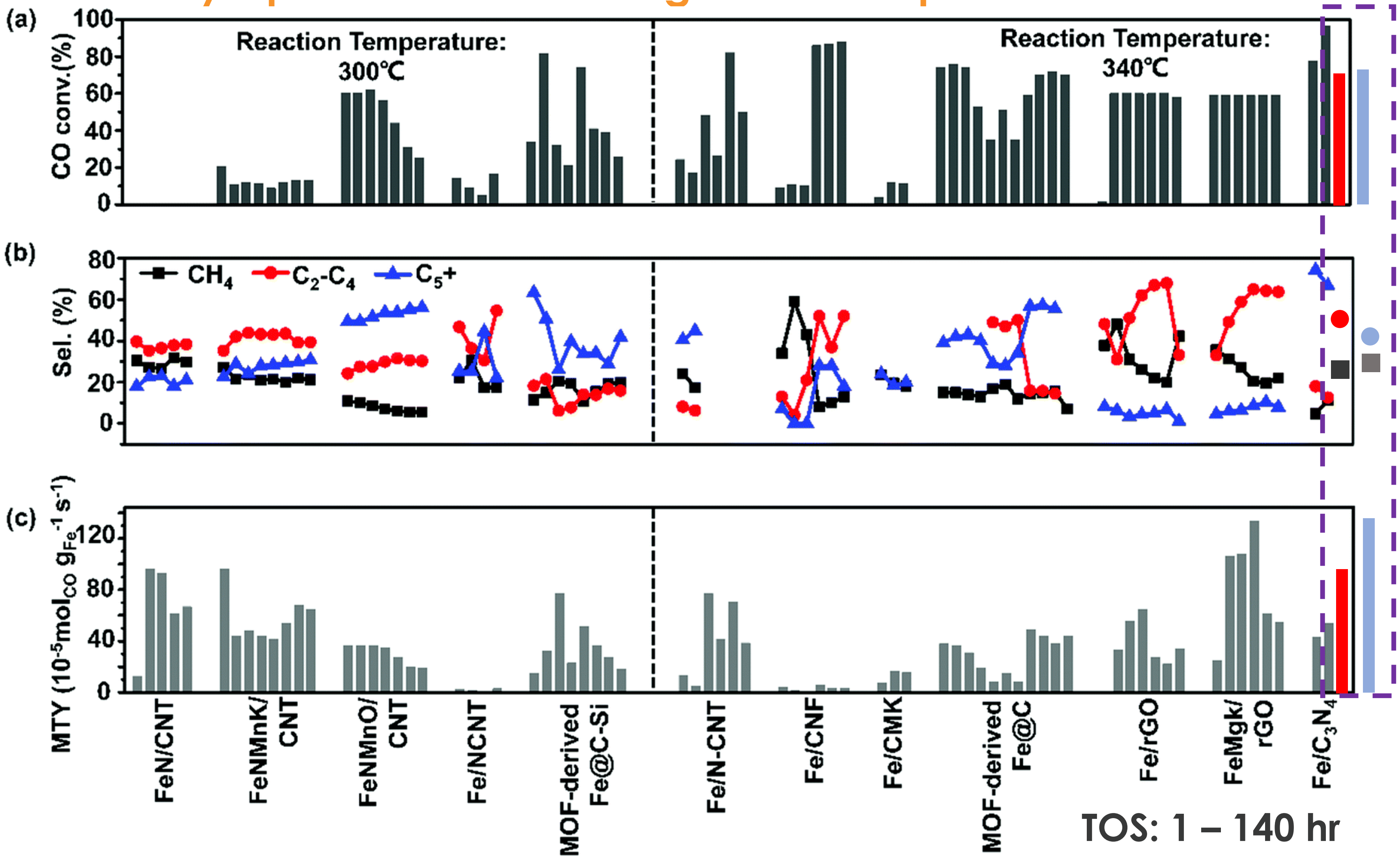




Catalyst selectivity for olefins surpasses previous NETL catalyst and maintains high selectivity for 400 h TOS.

Comparing Fe/C Technology to SOTA

Overall catalyst performance among the best reported in the literature



2021 and 2016 NETL catalysts at 90 hr TOS

O/P ratio: **4.91** vs 3.45

Chem. Soc. Rev., **50**, 2337-2366 (2021).

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Modular NG to Olefins Process Model and TEA

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Status:

- Susteon leading process development/modeling effort as part of its in-kind contributions to CRADA agreeement
- Experimental mass/energy data sets are being generated (data presented earlier) from plasma set up at SHU and the Fe/C reaction studies at NETL.
- Initial process model was set up in Aspen. Detailed model will be developed as datasets become available.

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Next Steps

- **Catalyst stability is #1 technical challenge & project risk**
  - We have identified pathways to address this new & unexpected challenge
    - Methods for controlling K content
    - Returning to "small batch" synthesis and completing study with this catalyst instead of "scaled up synthesis" approach.
    - Future work will **REQUIRE** us to dive deeper into catalyst stability/regeneration issues
  - We anticipate being able to initiate TEA with current results
- **Process Modeling & TEA Study will be started using experimental inputs from plasma and catalyst study**
- **Go/No-Go Milestone, 10/1/2021: Complete process modeling study and provide preliminary TEA. If manufacturing costs are 25% lower, or better, project is expected to move forward.**

APPENDIX

Natural Gas to Syngas w/Plasma Reactor System

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Steam Methane Reformation

$CH_4 + H_2O \rightarrow 3H_2 + CO$

Catalytic Non-Thermal Plasma (CNTP) reactor developed in collaboration with Susteon

Mixed Steam Methane Reformation

$2CH_4 + H_2O + CO_2 \rightarrow 5H_2 + 3CO$

Steam Methane Reforming Summary

Operational Parameters						Efficiency Parameters		
H_2O/CH_4	Temp	CH_4 Res Time	Plasma Voltage			CH_4 Conversion, %	H_2 Selectivity, %	CO Selectivity, %
Mol/mol	°C	s	V					
4.0	460	6	15,000		No Plasma	32.8	96.9	1.7
					Plasma 15.0kV	48.7	92.9	5.1

Mixed Methane Reforming Summary

Operational Parameters						Efficiency Parameters		
H_2O/CH_4	Temp	CH_4 Res Time	Plasma Voltage			CH_4 Conversion, %	H_2 Selectivity, %	CO Selectivity, %
Mol/mol	°C	s	V					
4.0	460	6	15,000		No Plasma	33.1	95.7	1.8
					CO_2 feed ON, NO Plasma	29.0	94.9	3.2
					CO_2 feed ON Plasma 15 kV	42.3	93.1	7.3

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Natural Gas to Syngas w/Plasma Reactor System

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Steam Methane Reformation with CNTP reactor to generate Syngas

Catalytic Non-Thermal Plasma (CNTP) reactor developed in collaboration with Susteon

Steam Methane Reformation

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

Mixed Steam Methane Reformation

$$2CH_4 + H_2O + CO_2 \rightarrow 5H_2 + 3CO$$

Table 1. Syngas synthesis by thermo-catalytic conversion of methane and steam with & w/out plasma discharge. Ratio of H_2O/Methane is 4:1, methane residency time is 6s, catalyst charge (Clariant Reformax 330) = 20 cc. Electrical power supply voltage for plasma operation is 15 kV at a set frequency of 10 kHz.

Operational Parameters						Efficiency Parameters		
H_2O/CH_4	Temp	CH_4 Res Time	Plasma Voltage			CH_4 Conversion, %	H_2 Selectivity, %	CO Selectivity, %
Mol/mol	°C	s	V					
4.0	460	6	15,000		No Plasma	32.8	96.9	1.7
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Mol/mol	°C	s	V					
4.0	460	6	15,000		No Plasma	33.1	95.7	1.8
					CO_2 feed ON, NO Plasma	29.0	94.9	3.2
					CO_2 feed ON Plasma 15 kV	42.3	93.1	7.3

Table 2. Mixed process for Syngas production by thermo-catalytic conversion of CO_2, CH_4 and H_2O with & w/out plasma discharge. Ratio of H_2O/CH_4 is 4:1, ratio of CO_2 /CH_4 = 1:2, residence time is 6s, and catalyst charge (Clariant Reformax 330) = 20 cc. Electrical power supply voltage for plasma operation is 15kV at a set frequency of 10 kHz.

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Natural Gas to Syngas w/Plasma Reactor System

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Dry Methane Reformation with CNTP reactor to generate Syngas

Dry Methane Reformation

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$$

Table 3. Syngas production by thermo-catalytic conversion of CO_2 and CH_4 with & w/out plasma discharge. Ratio of CH_4 and CO_2 = 1, residence time is 6s, catalyst charge (Johnson Matthey CP1444) = 20 cc. Electrical power supply voltage to generate plasma is 15 kV and 17 kV at a set frequency of 10 kHz.

Operational Parameters						Efficiency parameters		
H_2O/CH_4	**Temp**	**CH_4 Res Time**	**Plasma Voltage**		**CH_4 Conversion, %**	**CO_2 Conversion, %**	**H_2 Selectivity, %**	**CO Selectivity, %**
Mol/mol	**^oC**	**s**	**V**					
4.0	**200**	**6**	**No plasma**		**3.3**	**10.8**	**1.8**	**8.6**
			15,000		**13.4**	**8.0**	**36.2**	**66.8**
			17,000		**40.5**	**20.8**	**40.7**	**50.2**

Reference Data Files (Year 2021):
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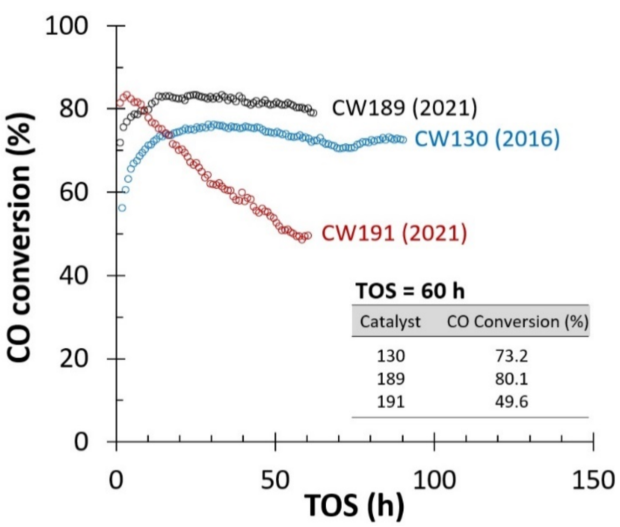
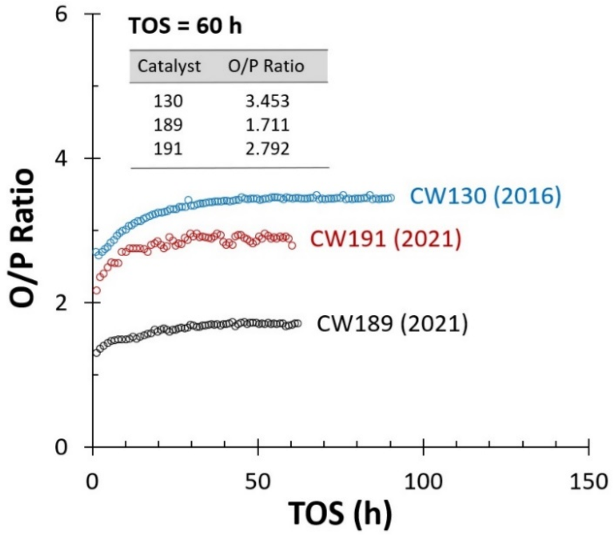
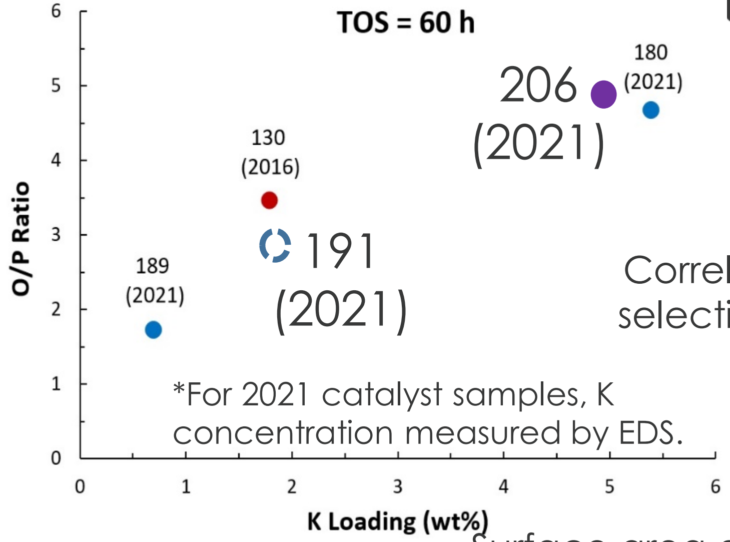
Syngas to Olefins w/Nanostructured Fe/C



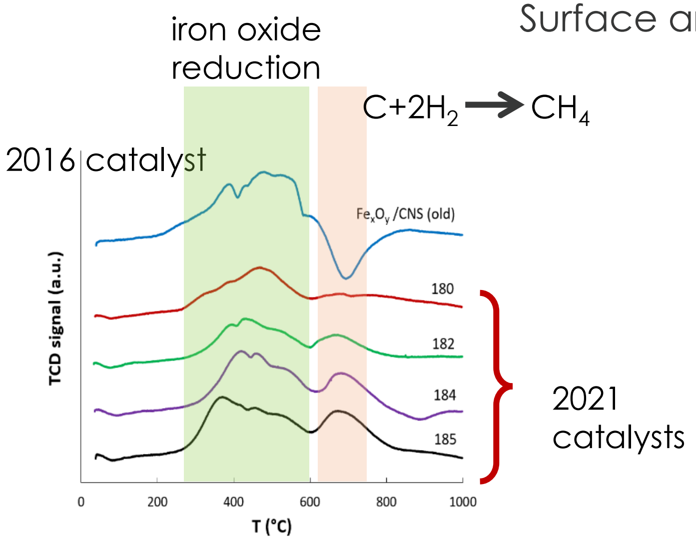


Many recent catalysts show lower selectivity (O/P ratio) and/or activity/stability



Correlation of K and selectivity (O/P ratio)

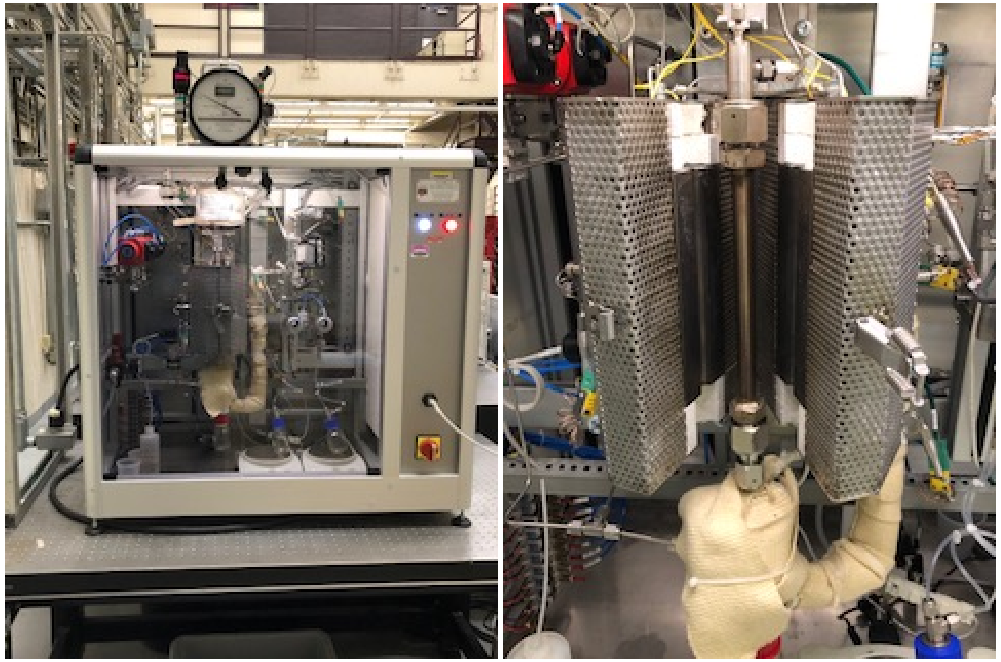
Surface area of 2016 (130) catalyst: 81 m
Surface area of 2021 catalysts: ~1,000 m



Clear differences from previous catalysts and K concentration an important parameter – better control of synthesis conditions.

FTO Testing

FT Unit



Testing Protocol

1. Activation

Catalyst weight	200 mg
Temperature	400 °C
Pressure	1 bar
Reducing gas	UHP H_2
Flow rate	50 sccm
Reduction time	3 h

2. Cooling

Temperature	350 °C
Cooling gas	UHP N_2
Flow rate	50 sccm

3. Reaction

Temperature	350 °C
Pressure	20 bar
Feed gas	13/30/45% CO, 13/60/45% H_2, 74%/10% N_2
Flow rate	100 sccm
WHSV	30,000 cc/g_{cat}/h
Time on stream	>300 h