NREL
Transforming ENERGY

Shifting the paraffin-to-olefin ratio and gasoline fuel properties with bimetallic BEA zeolite catalysts in dimethyl ether homologation

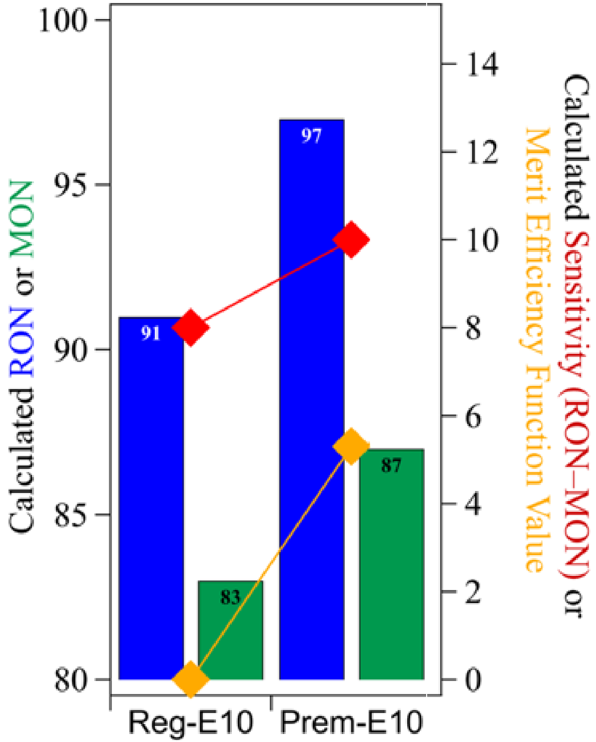
Connor Nash, Daniel Dupuis, Carrie Farberow, Anh To, Anurag Kumar, Ce Yang, Evan Wegener, Jeffrey Miller, Kinga Unocic, Jesse Hensley, Joshua Schaidle, Susan Habas, Daniel Ruddy

2019 AIChE Annual Meeting
Thursday, November 14, 2019
Orlando, Florida


Plus
Premium
Biofuel
MINIMUM OCTANE RATING
(R + M)/2 METHOD
89
MINIMUM OCTANE RATING
(R + M)/2 METHOD
100
PUSH
TO
PUSH
TO
START
PUSH
TO
START

Comparing Fuel Properties with Merit Efficiency

RON = Research Octane Number
MON = Motor Octane Number



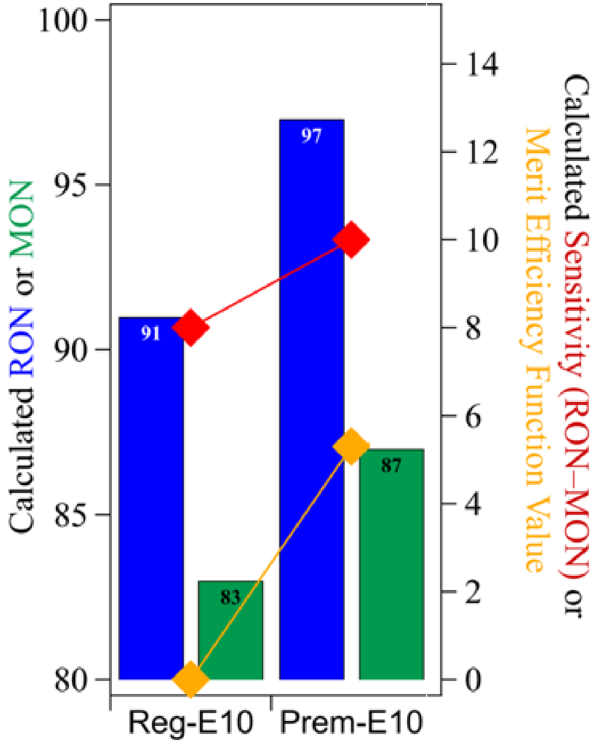
Comparing Fuel Properties with Merit Efficiency

RON = Research Octane Number
MON = Motor Octane Number

$$\text{Merit Efficiency Function} = \frac{\overbrace{(RON - 91)}^{\uparrow RON} + 1.25\overbrace{(S - 8)}^{\uparrow S > 8\ (\uparrow RON,\ \downarrow MON)}}{1.6}$$

Sensitivity = RON – MON

Regular-E10 gasoline defined as 0 → RON = 91, S = 8
Premium-E10 gasoline = 5.3



Miles, P., Technical Report U.S. Department of Energy, Washington, D.C., 2018.

Comparing Fuel Properties with Merit Efficiency

Merit Efficiency Function

$$= \frac{(\text{RON} - 91) + 1.25(\text{S} - 8)}{1.6}$$

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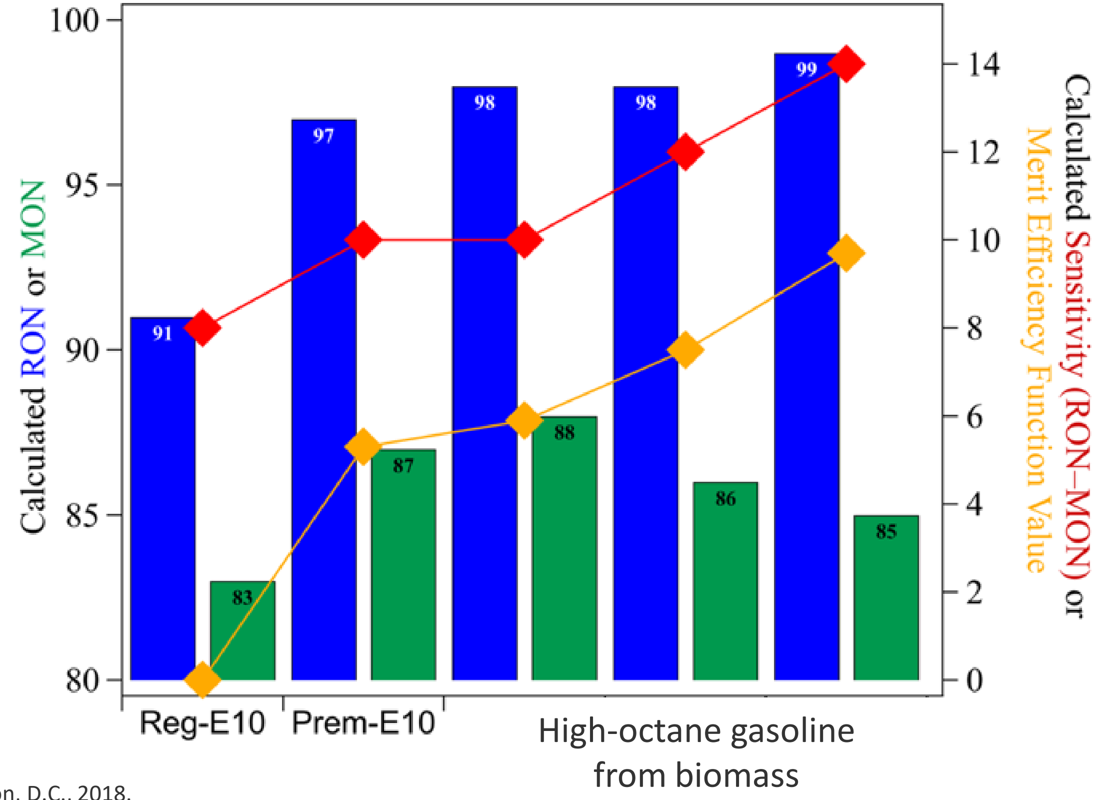


Miles, P., Technical Report U.S. Department of Energy, Washington, D.C., 2018.

High-Octane Fuels from Biomass, DME Homologation

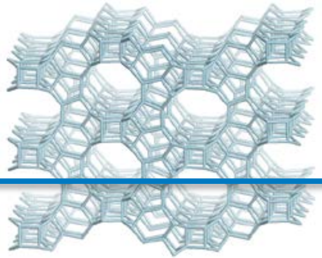
Biomass or Waste → Gasification → **Syngas $H_2 + CO$** → CuZnO Al_2O_3 → **Methanol & Dimethyl Ether** → Zeolite Catalysts → **High Octane Gasoline**

Dimethyl Ether (DME)

$H_3C-O-CH_3$

Mild process conditions

175-225°C, 1-10 atm

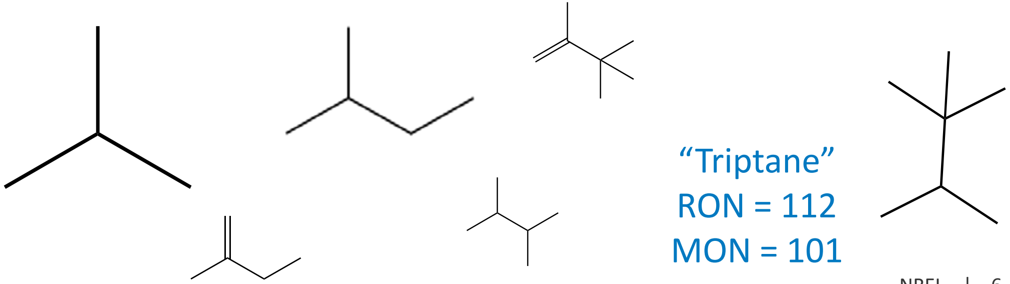


Large-pore acidic zeolites

HBEA, Cu/BEA

Branched Hydrocarbons

C_4 — C_7



"Triptane"
RON = 112
MON = 101

Branched olefin content increases RON and S

High Merit Efficiency Gasoline

RON > 90

S > 8

	Paraffins				Olefins		
Compound	RON	MON	S	Compound	RON	MON	S
Iso-pentane	92	90	2	Iso-pentenes	103	82	21
Dimethyl-C_6	99	94	5	Iso-hexenes	100	83	17
Dimethyl-C_7	94	90	4	C_7-enes	90	78	12
Trimethyl-C_8	105	99	6	C_8-enes	90	77	13
Triptane	112	101	11				

Ghosh, P., K.J. Hickey, and S.B. Jaffe. Ind. Eng. Chem. Res., 2006.

Branched olefin content increases RON and S

High Merit Efficiency Gasoline

RON > 90

S > 8

Decrease P:O ratio to increase S and Merit Efficiency

Paraffins				Olefins			
Compound	**RON**	**MON**	**S**	**Compound**	**RON**	**MON**	**S**
Iso-pentane	92	90	2	Iso-pentenes	103	82	21
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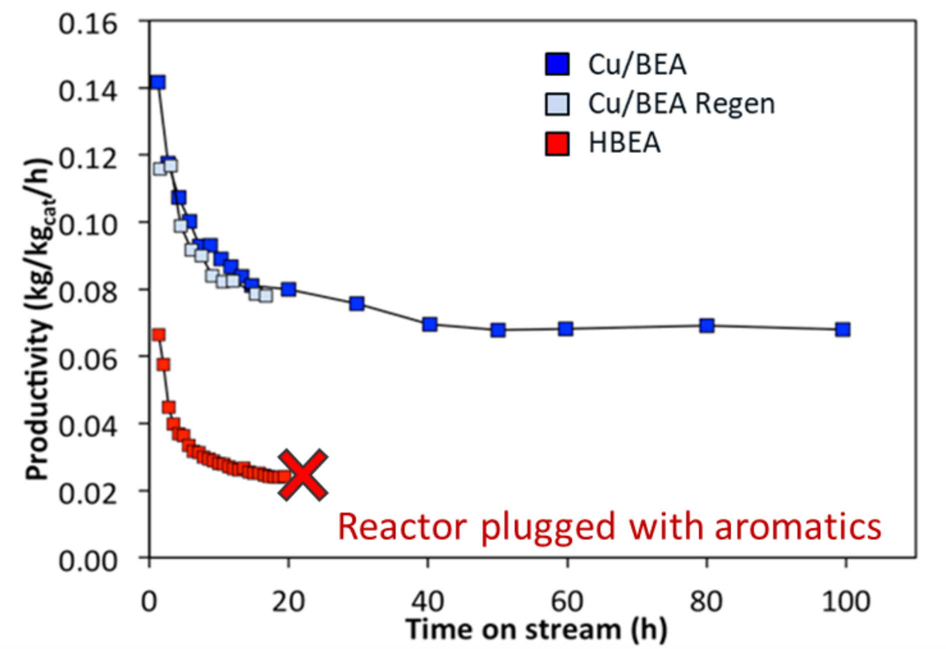
Triptane	112	101	11				

Ghosh, P., K.J. Hickey, and S.B. Jaffe. Ind. Eng. Chem. Res., 2006.

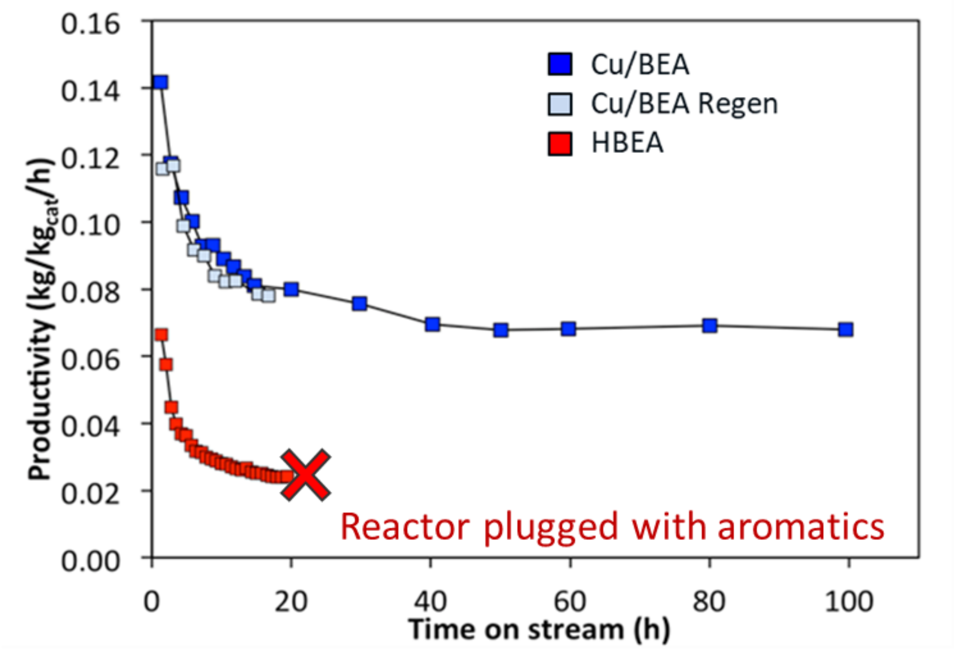
Metallic Cu/BEA improves productivity and lifetime

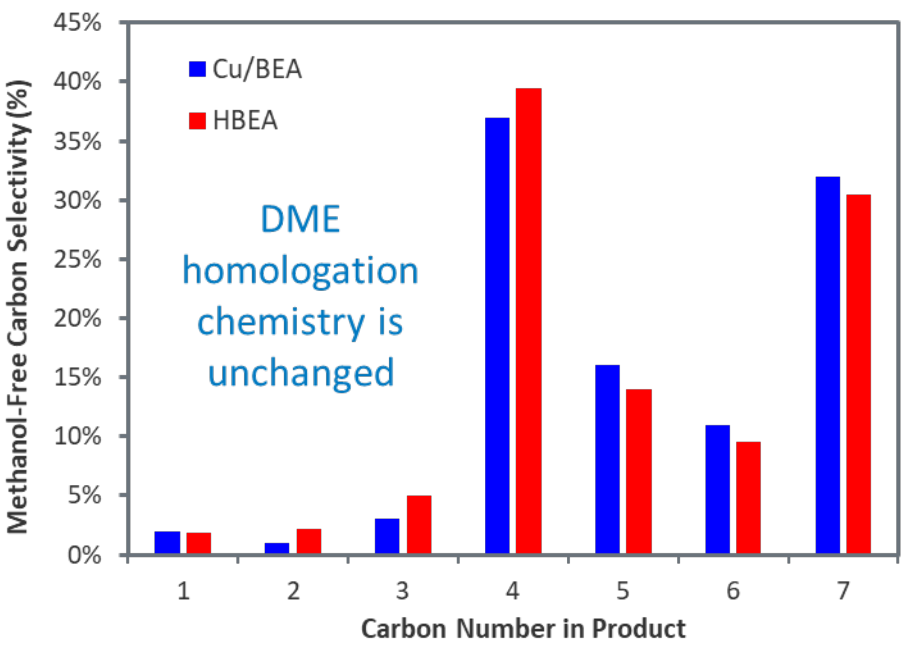


Ruddy, D.A., et al., Nature Catalysis, 2019.

US Pat # 9,714,387 B2 US Pat # 9,803,142 B1 US Pat # 9,796,931 B1

Metallic Cu does not affect HBEA chemistry





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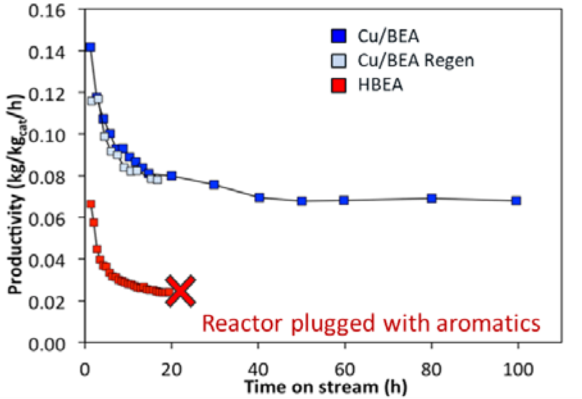
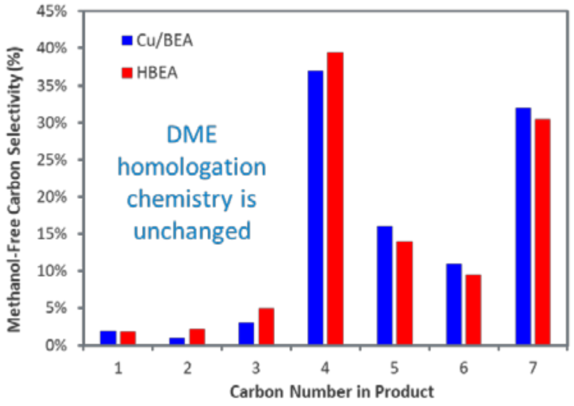
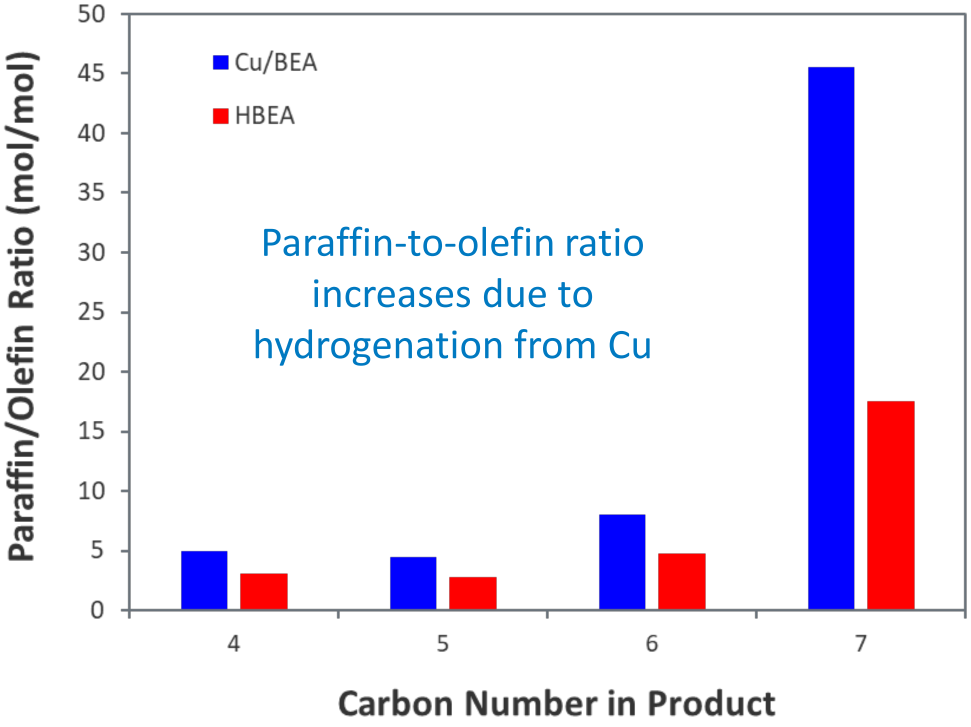
Cu increases paraffin content via hydrogenation







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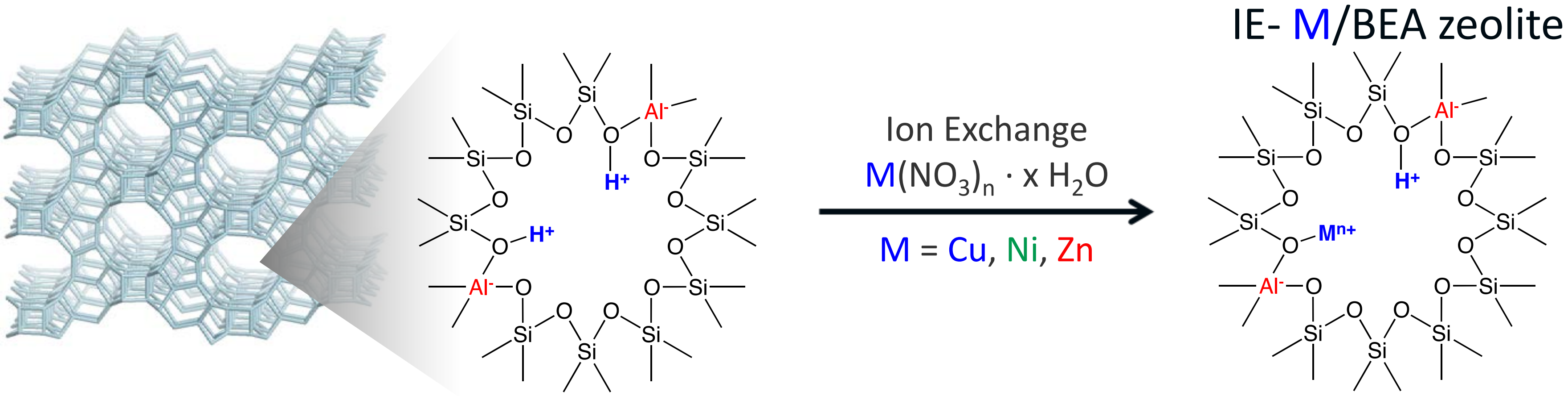
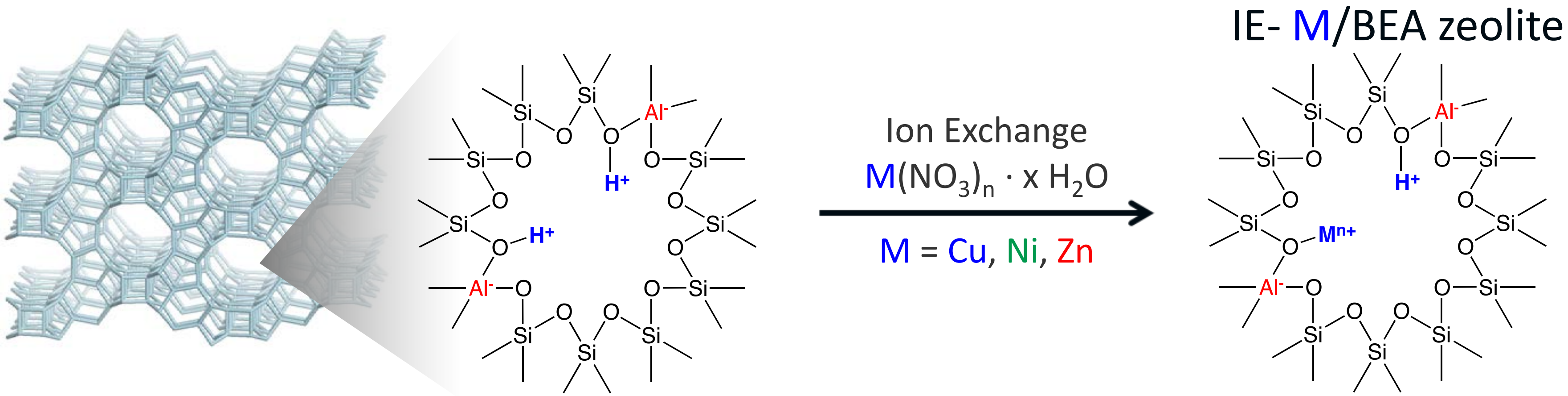
Dehydrogenation with Ion-Exchanged M-BEA

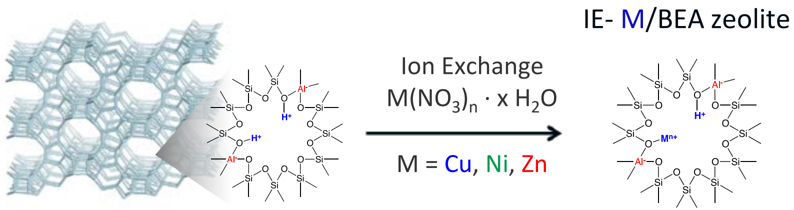


Dehydrogenation with Ion-Exchanged M-BEA



Catalyst	Metal loading (wt%, μmol/g_{cat})	M oxidation state
IE-Cu/BEA	0.876, 138	1+
IE-Ni/BEA	0.792, 135	2+
IE-Zn/BEA	1.00, 153	2+

Dehydrogenation with Ion-Exchanged M-BEA



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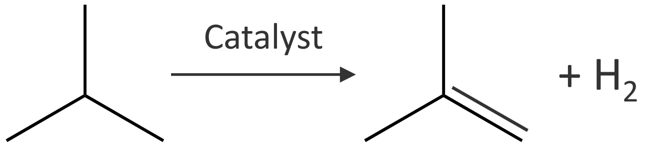
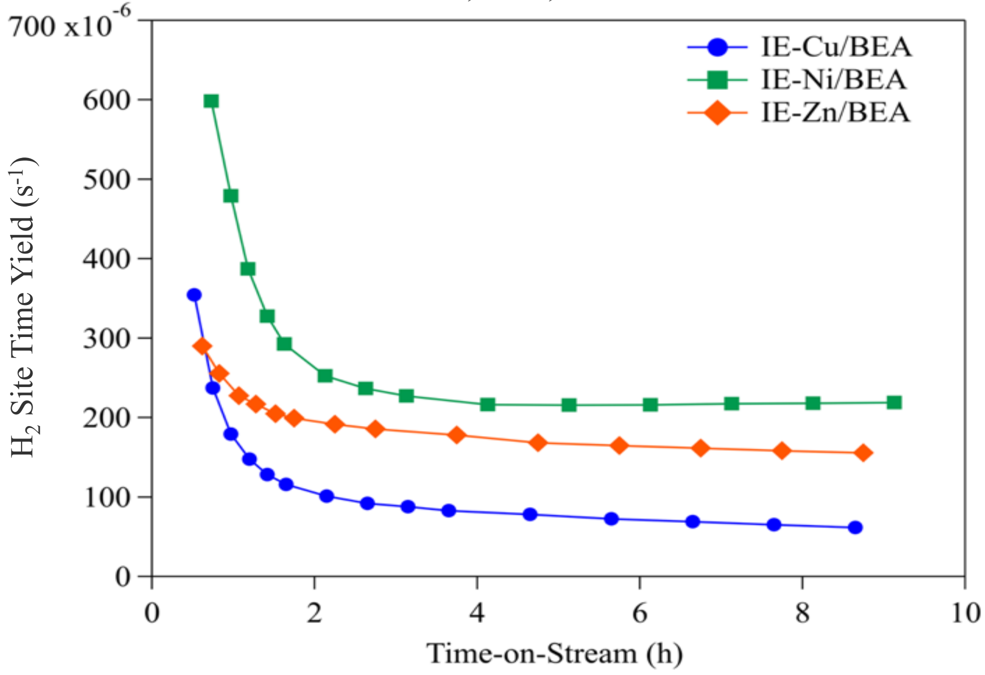
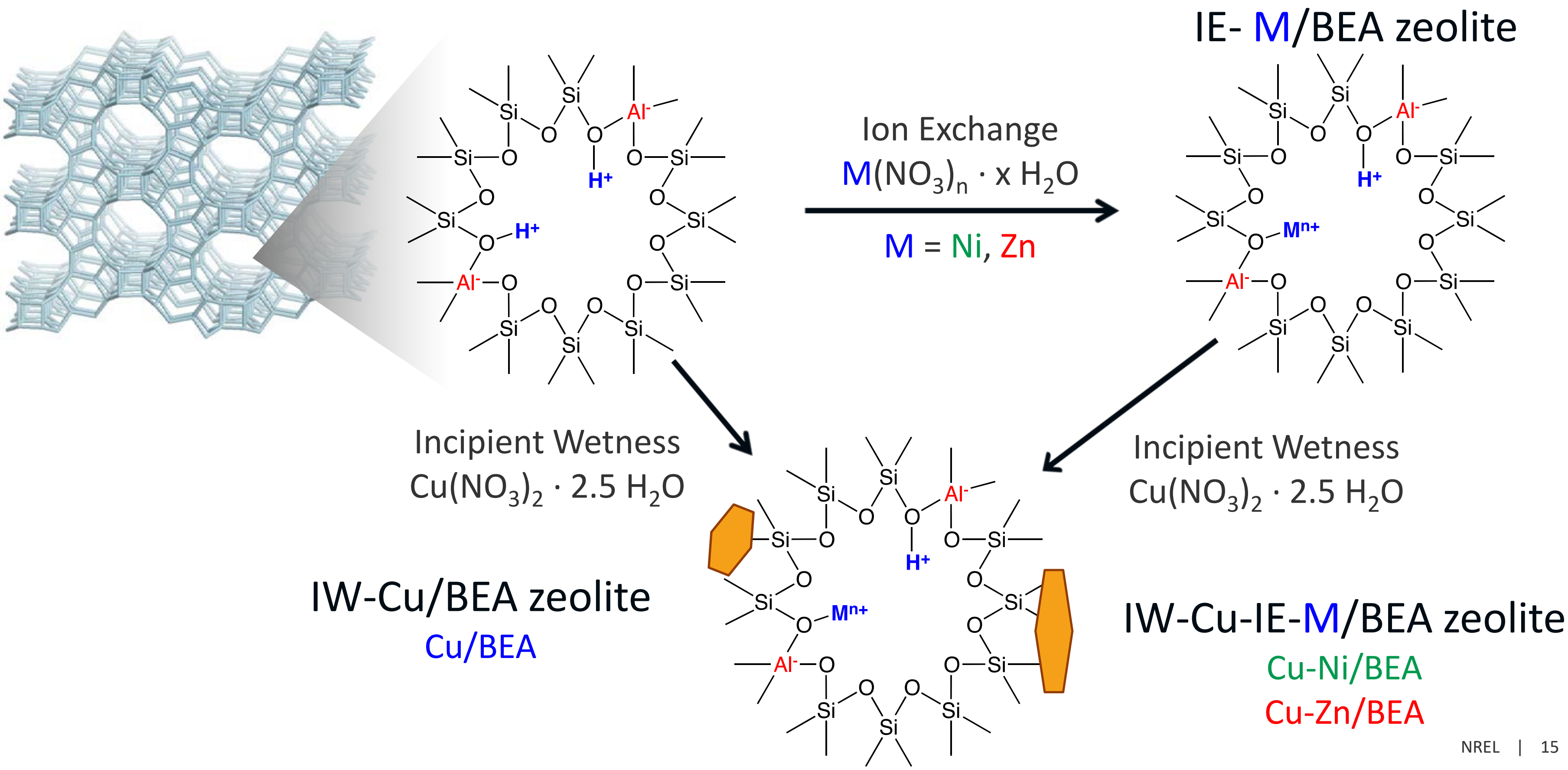


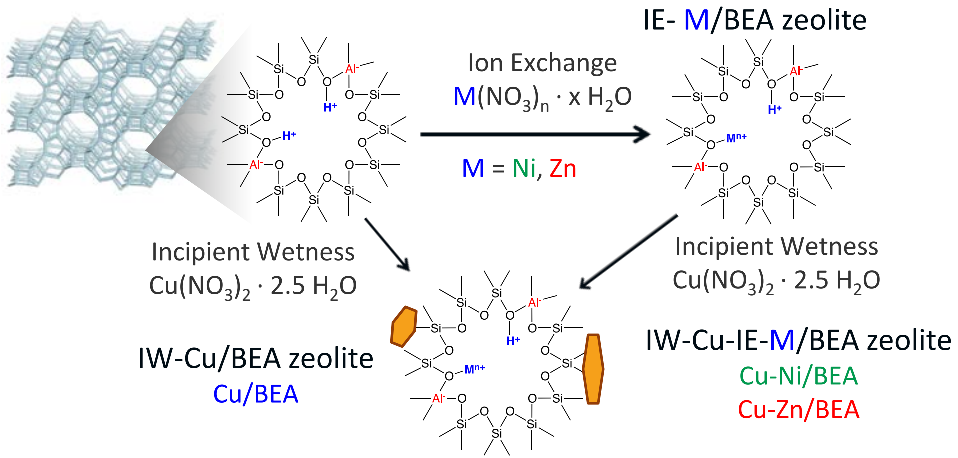
Conditions: 300 °C, 2 atm, Isobutane WHSV = 0.1 h^{-1}



2-Step Bimetallic Catalyst Synthesis

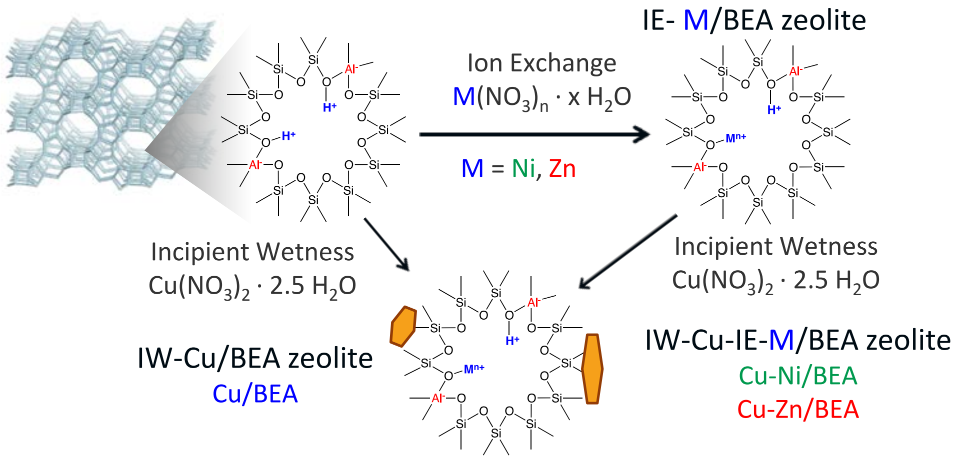


Bimetallic Catalyst Characterization



Catalyst	Metal loading (wt% Cu; M)	Ionic Cu (%)	Metallic Cu (%)	Ionic Zn (%)	Ionic Ni (%)	Metallic Ni (%)
Cu/BEA	4.3	14	86	–	–	–
Cu-Ni/BEA	4.6; 0.71	0	100	–	88	12
Cu-Zn/BEA	4.3; 0.77	8	92	100	–	–

Bimetallic Catalyst Characterization



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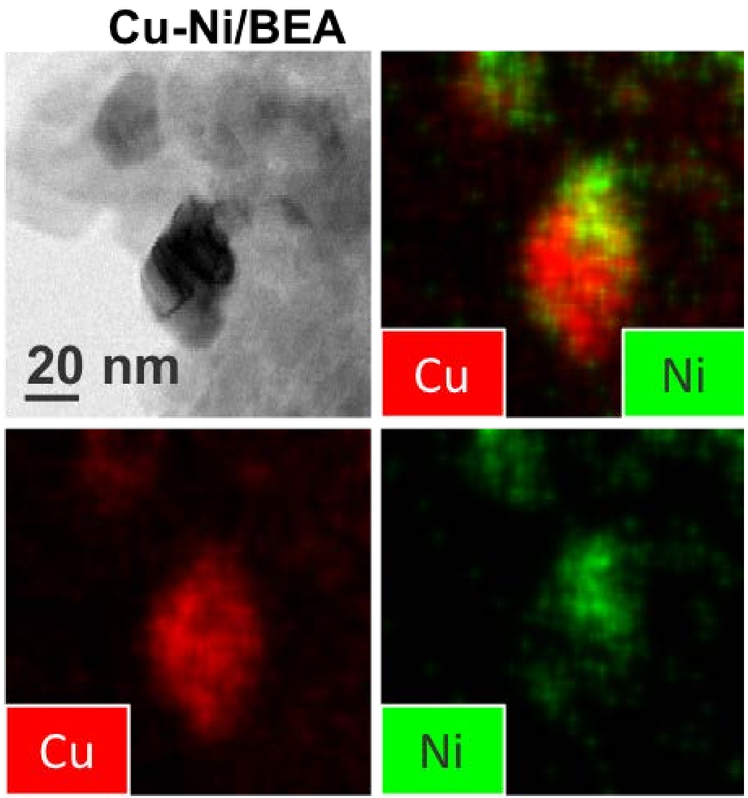
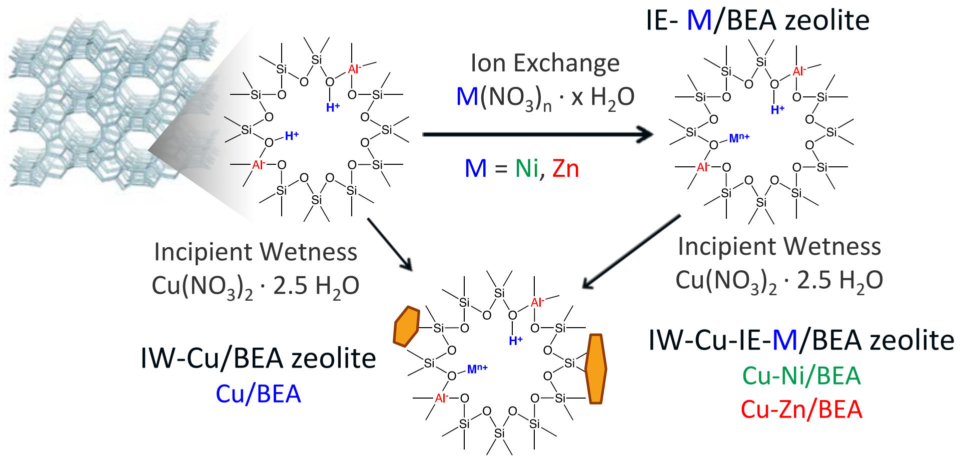
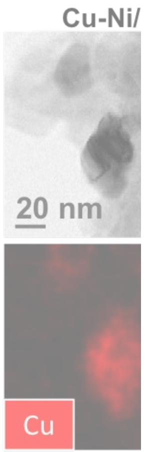
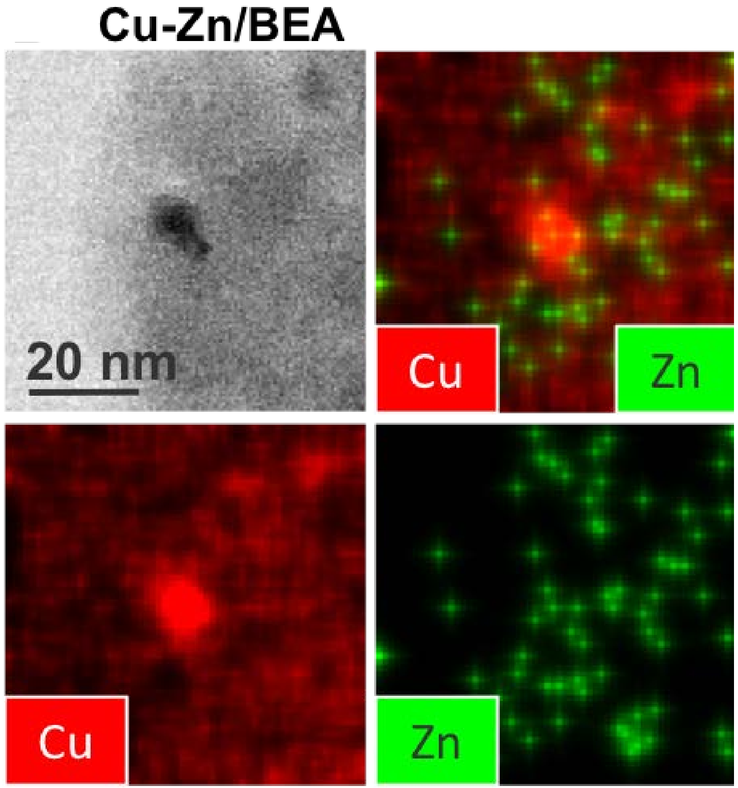


Bimetallic Catalyst Characterization







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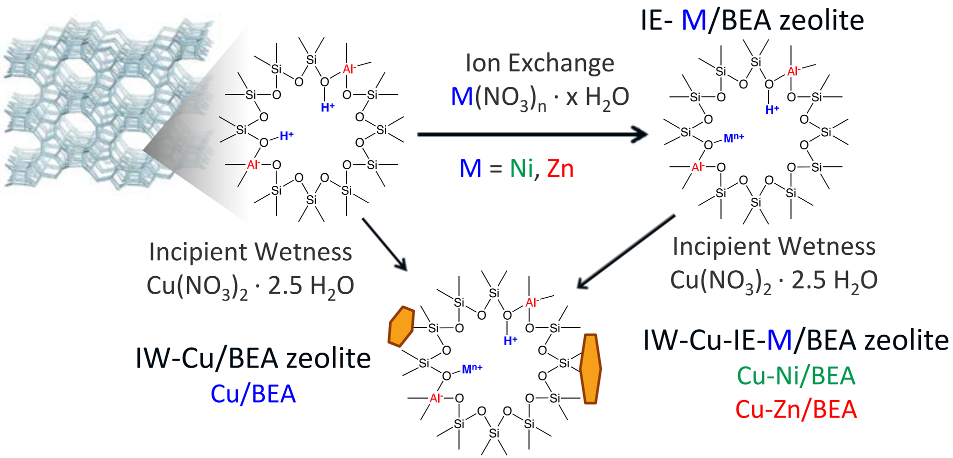
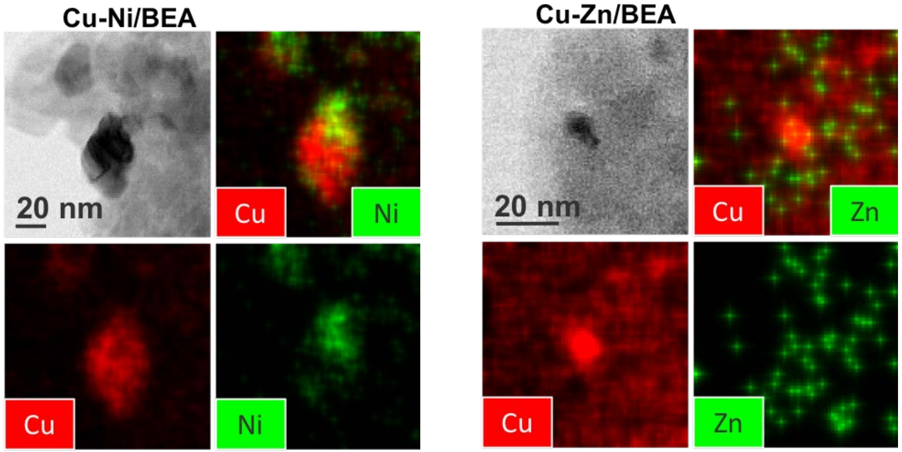
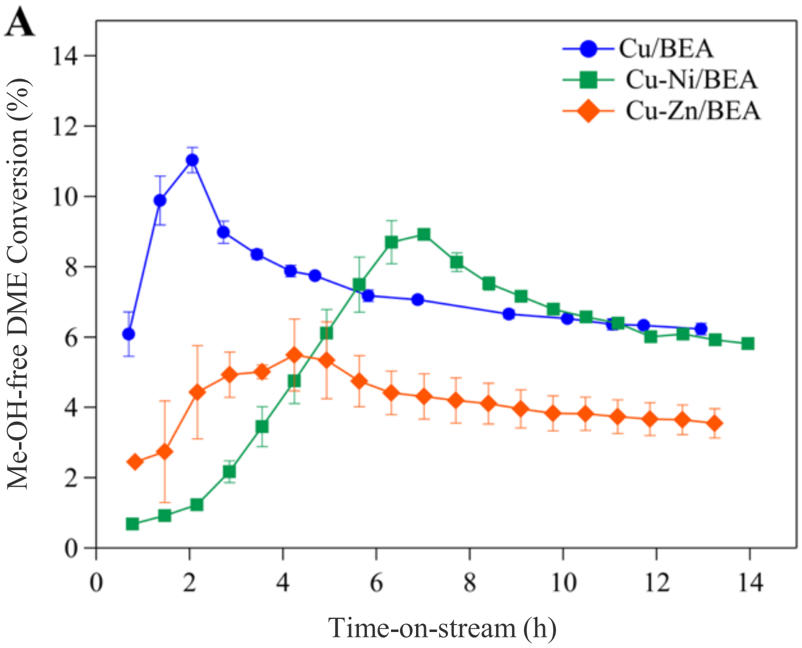
Bimetallic Catalyst Characterization





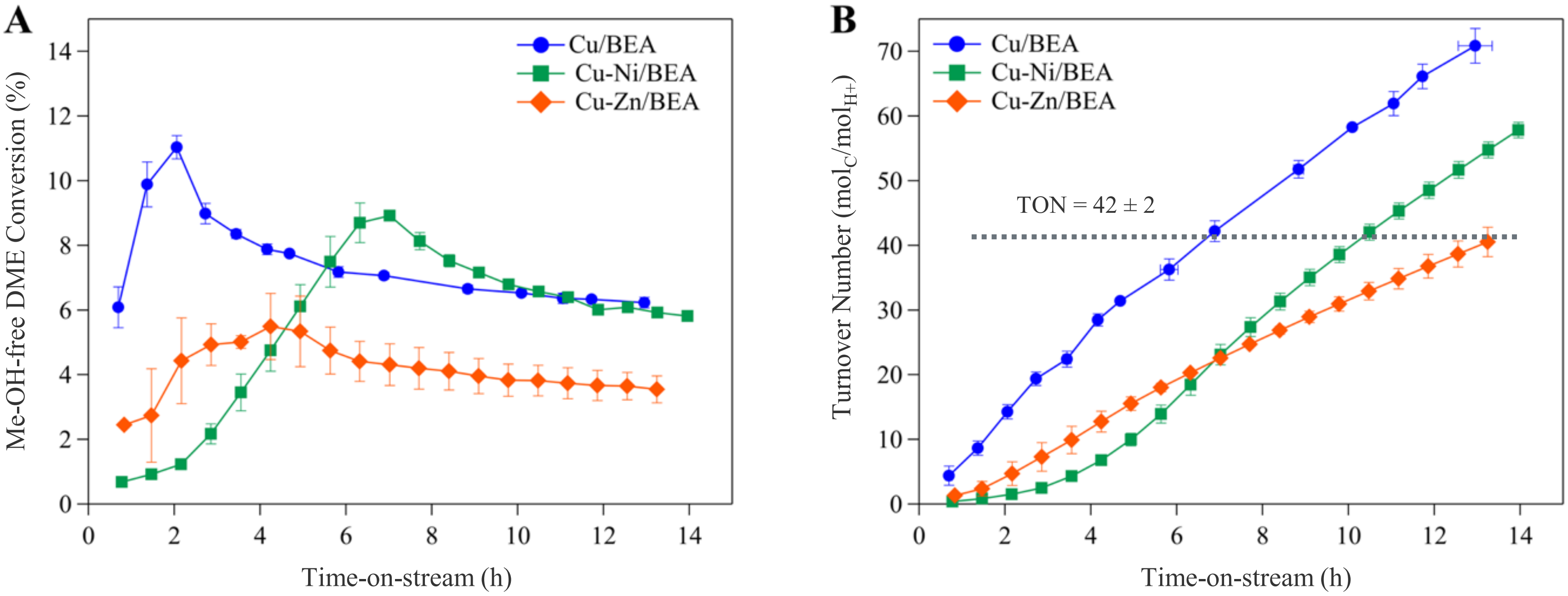
Catalyst	Metal loading (wt% Cu; M)	Ionic Cu (%)	Metallic Cu (%)	Ionic Zn (%)	Ionic Ni (%)	Metallic Ni (%)	Acid site density (µmol/g)	B site density (µmol/g)	L site density (µmol/g)	B/L ratio (mol/mol)
Cu/BEA	4.3	14	86	–	–	–	1770	1230	540	2.3
Cu-Ni/BEA	4.6; 0.71	0	100	–	88	12	1710	1210	500	2.4
Cu-Zn/BEA	4.3; 0.77	8	92	100	–	–	1660	1210	450	2.7

Bimetallic Activity



Pretreatment: 300 °C H_2 reduction for 2 h
Conditions: 200 °C, 1 atm, DME WHSV = 2.2 h^{-1}, H_2:DME = 1:1

Bimetallic Activity



Pretreatment: 300 °C H_2 reduction for 2 h
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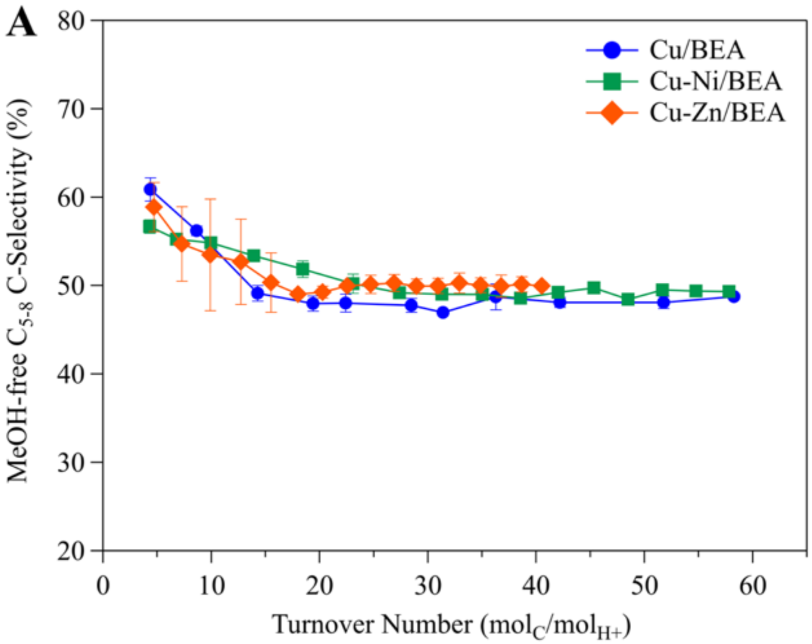
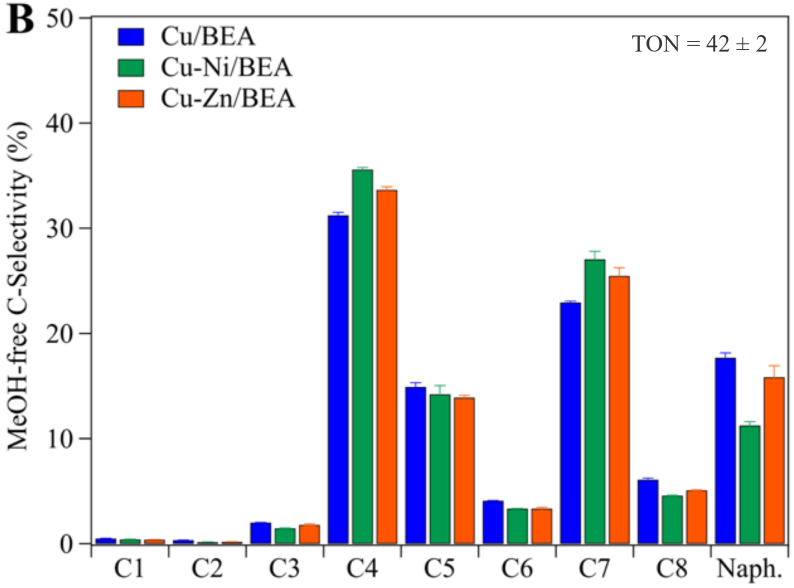
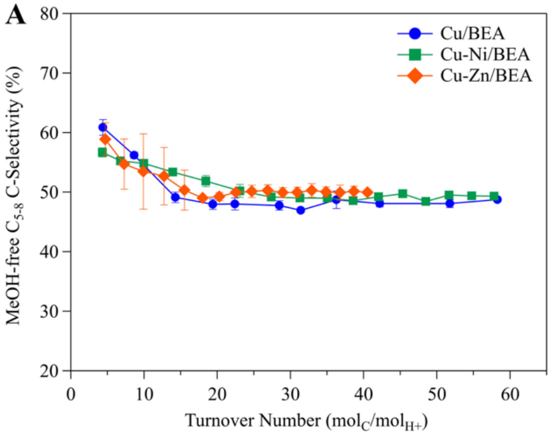
Bimetallic selectivity is comparable to Cu/BEA

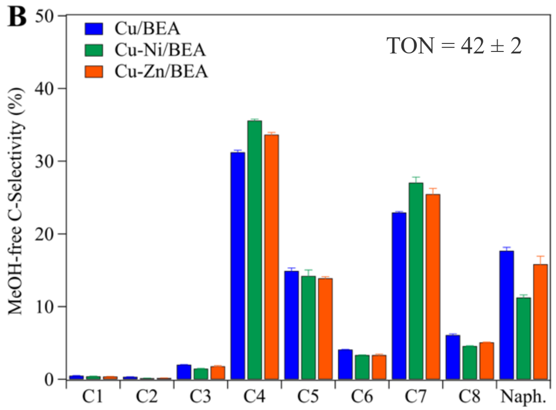


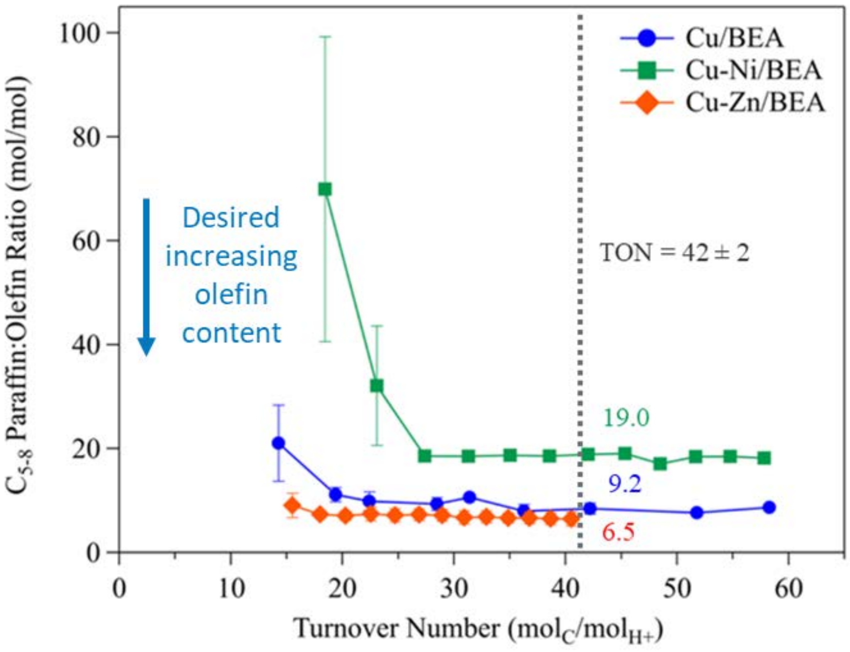


Pretreatment: 300 °C H_2 reduction for 2 h
Conditions: 200 °C, 1 atm, DME WHSV = 2.2 h^{-1}, H_2:DME = 1:1

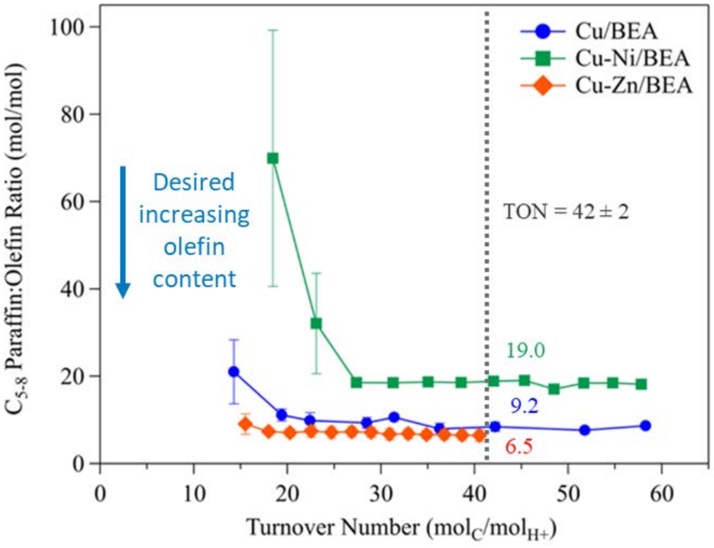
P:O increases for Ni, decreases for Zn

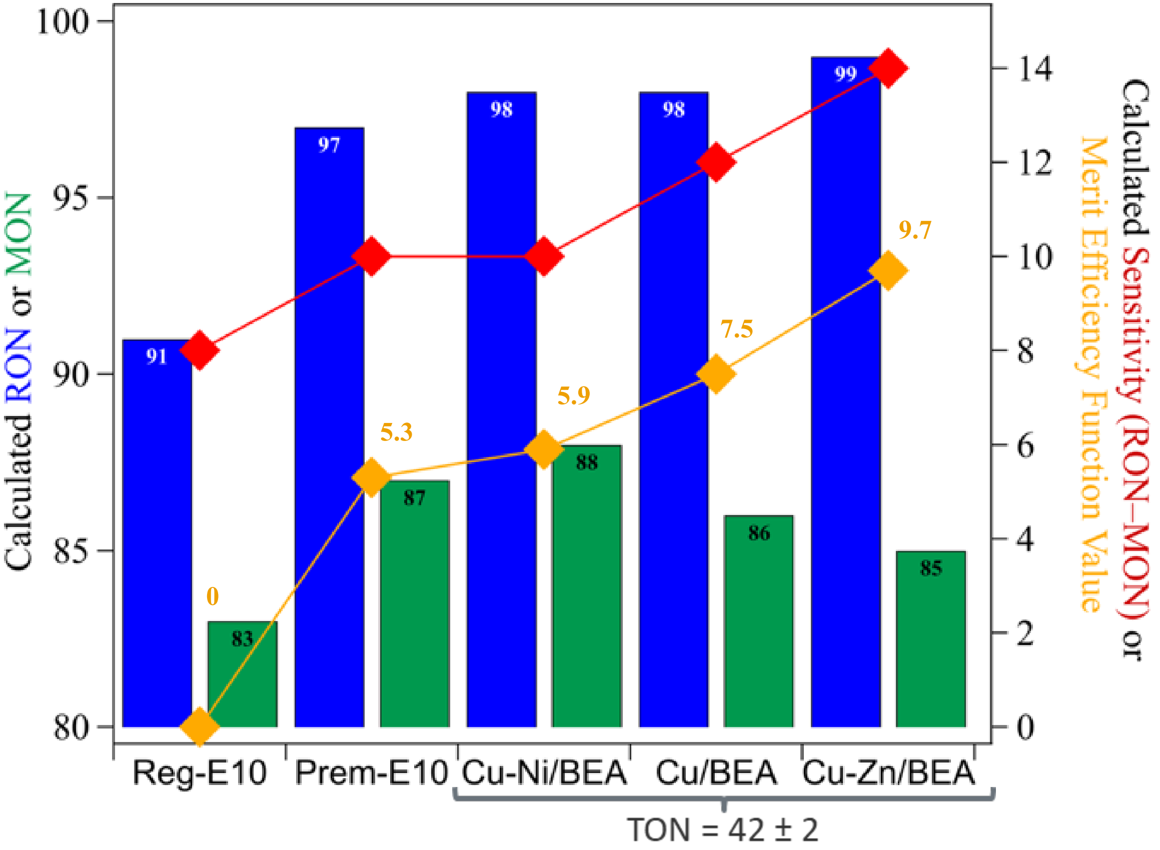




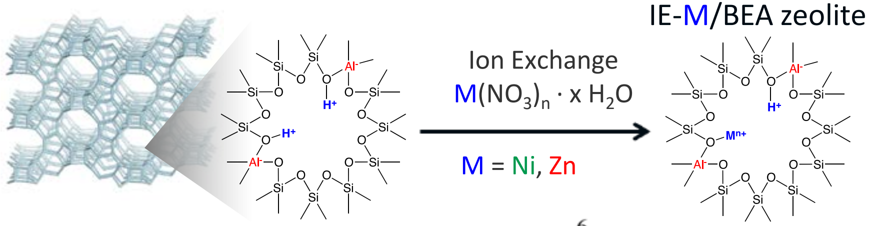


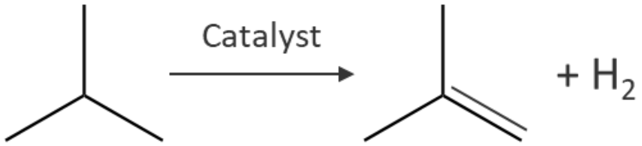
Estimated Fuel Properties

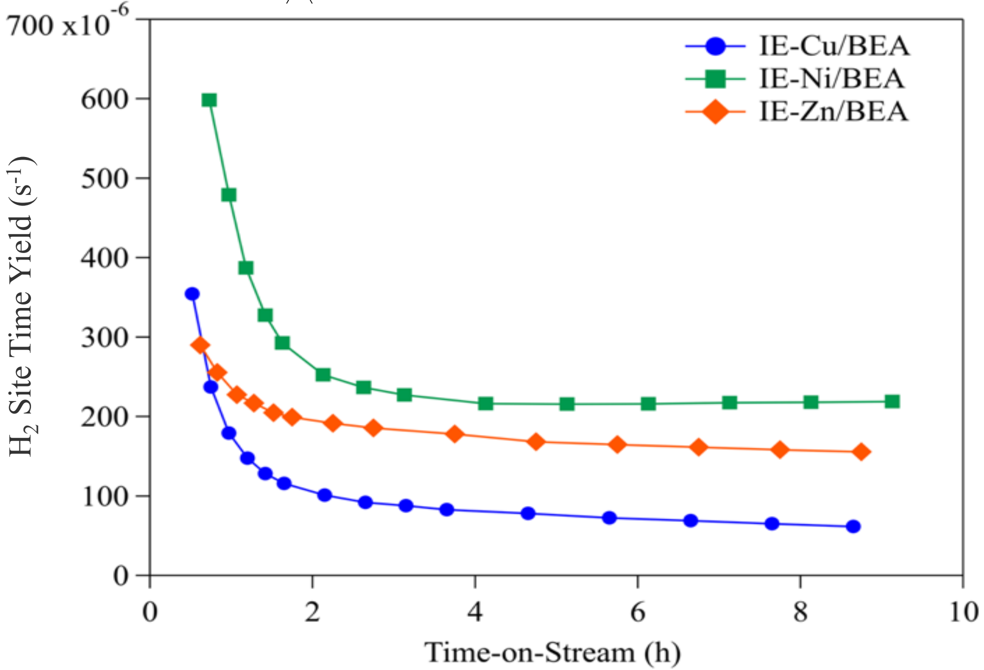




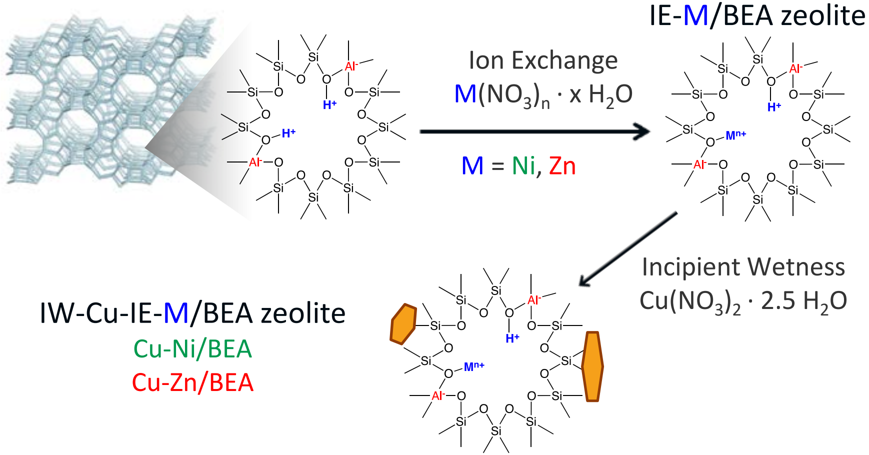
Closing


IE-M/BEA zeolite
Ion Exchange
M(NO3)n · x H2O
M = Ni, Zn
H+
Al-
Mn+

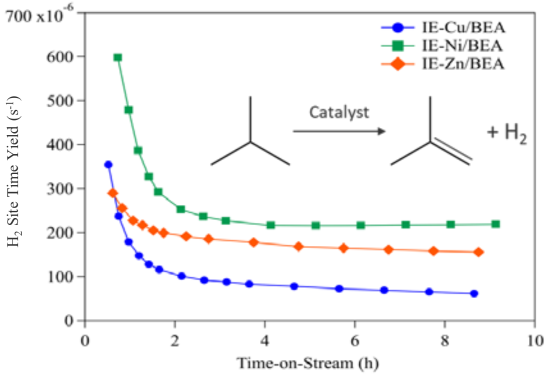

Catalyst
+ H2


IE-Cu/BEA
IE-Ni/BEA
IE-Zn/BEA
H2 Site Time Yield (s-1)
700 x10-6
600
500
400
300
200
100
0
0
2
4
6
8
10
Time-on-Stream (h)

Closing

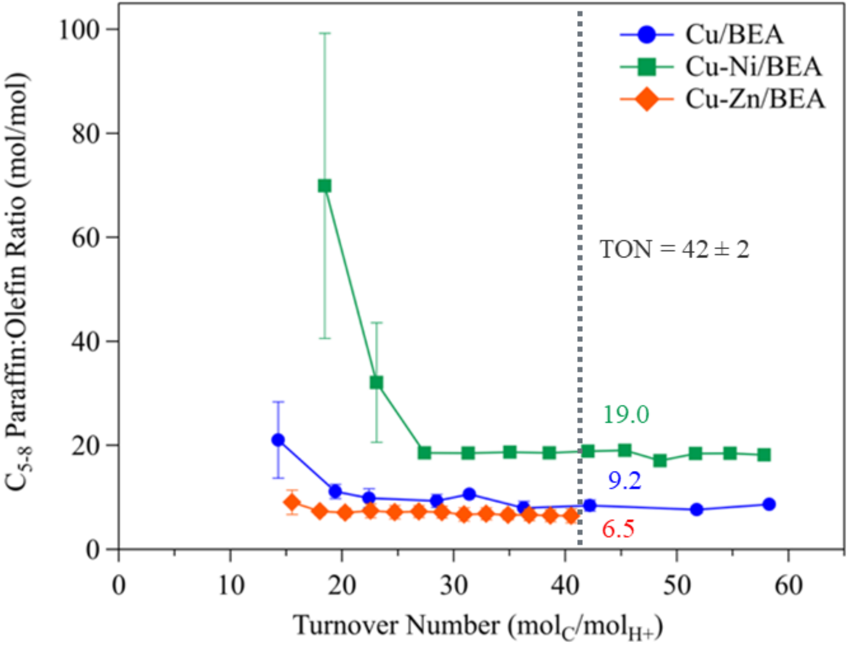


IE-M/BEA zeolite
Ion Exchange
$M(NO_3)_n \cdot x\ H_2O$
M = Ni, Zn
Incipient Wetness
$Cu(NO_3)_2 \cdot 2.5\ H_2O$
IW-Cu-IE-M/BEA zeolite
Cu-Ni/BEA
Cu-Zn/BEA



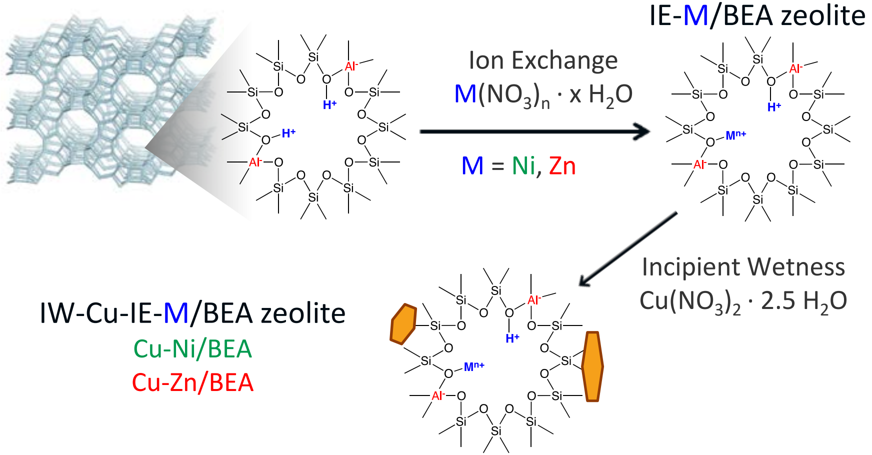
700 x10^-6
600
500
400
300
200
100
0
H2 Site Time Yield (s^-1)
0
2
4
6
8
10
Time-on-Stream (h)
IE-Cu/BEA
IE-Ni/BEA
IE-Zn/BEA
Catalyst
+ H2

DME
Catalyst
Hydrocarbons
H3C O CH3



100
80
60
40
20
0
C5-8 Paraffin:Olefin Ratio (mol/mol)
0
10
20
30
40
50
60
Turnover Number (molC/molH+)
Cu/BEA
Cu-Ni/BEA
Cu-Zn/BEA
TON = 42 ± 2
19.0
9.2
6.5

Closing



IE-M/BEA zeolite
Ion Exchange
$M(NO_3)_n \cdot x\ H_2O$
M = Ni, Zn
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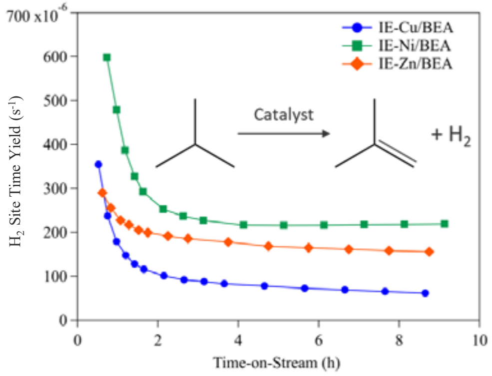
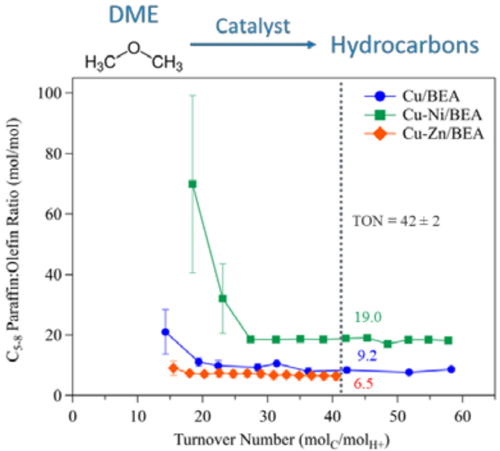
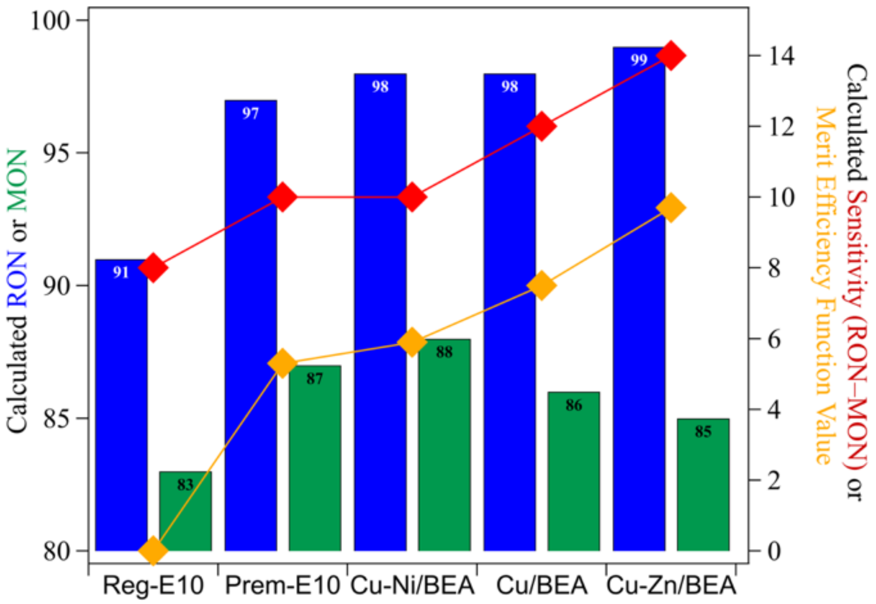
IW-Cu-IE-M/BEA zeolite
Cu-Ni/BEA
Cu-Zn/BEA



700 x10^{-6}
600
500
400
300
200
100
0
H_2 Site Time Yield (s^{-1})
0
2
4
6
8
10
Time-on-Stream (h)
IE-Cu/BEA
IE-Ni/BEA
IE-Zn/BEA
Catalyst
+ H_2



DME
$H_3C^{\frown O \frown}CH_3$
Catalyst
Hydrocarbons
100
80
60
40
20
0
C_{5-8} Paraffin:Olefin Ratio (mol/mol)
0
10
20
30
40
50
60
Turnover Number (mol$_C$/mol$_{H+}$)
Cu/BEA
Cu-Ni/BEA
Cu-Zn/BEA
TON = 42 ± 2
19.0
9.2
6.5



Calculated RON or MON
100
95
90
85
80
91
83
97
87
98
88
98
86
99
85
14
12
10
8
6
4
2
0
Calculated Sensitivity (RON–MON) or Merit Efficiency Function Value
Reg-E10
Prem-E10
Cu-Ni/BEA
Cu/BEA
Cu-Zn/BEA

Acknowledgements

NREL Catalyst Development Team

Jesse Hensley, Joshua Schaidle, Connor Nash, Carrie Farberow, Anh To, Dan Ruddy, Susan Habas, Matt Yung, Gary Grim, Anurag Kumar

Technoeconomic Analysis

Eric Tan, Abhijit Dutta

NREL Fuel Property Analysis

Earl Christensen

Argonne National Lab XAS Collaborators

Ted Krause, Jeff Miller, Evan Wegner, Ce Yang

Oak Ridge National Lab TEM Collaborators

Kinga Unocic

U.S. DEPARTMENT OF ENERGY

Bioenergy Technologies Office

DE-AC36-08-GO28308

ChemCatBio

Chemical Catalysis for Bioenergy

Energy Materials Network

U.S. Department of Energy

Thank you

What questions do you have?

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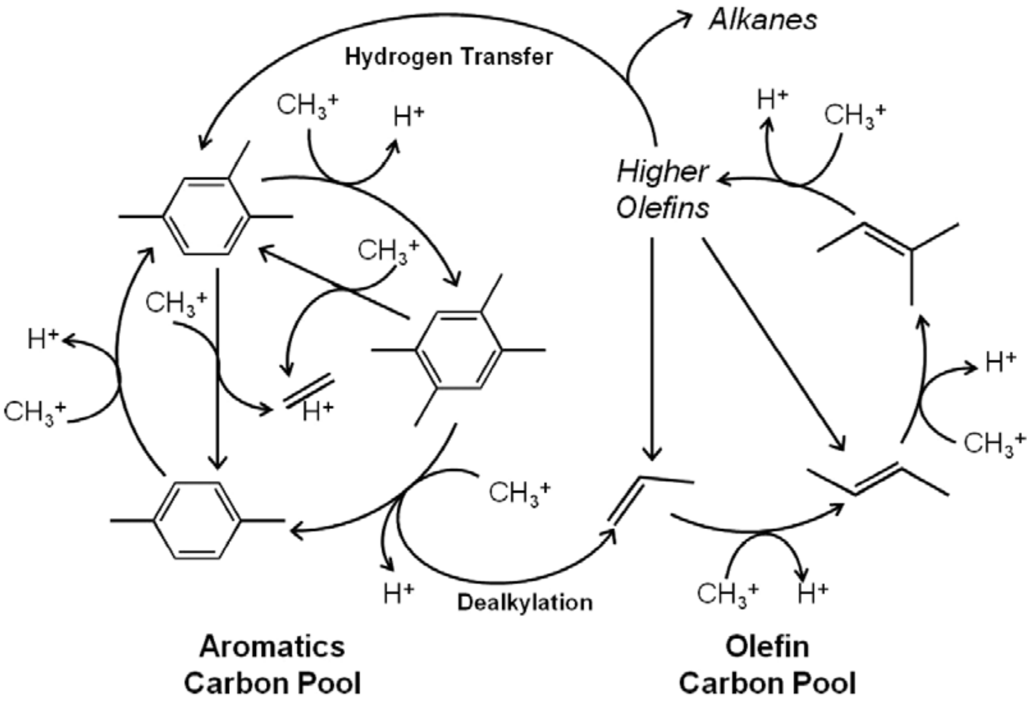
NREL/PR-5100-75386

This work was authored by Alliance for Sustainable Energy, LLC, the manager and operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies Office in collaboration with the Chemical Catalysis for Bioenergy (ChemCatBio) Consortium, a member of the Energy Materials Network (EMN). The views expressed in this work do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

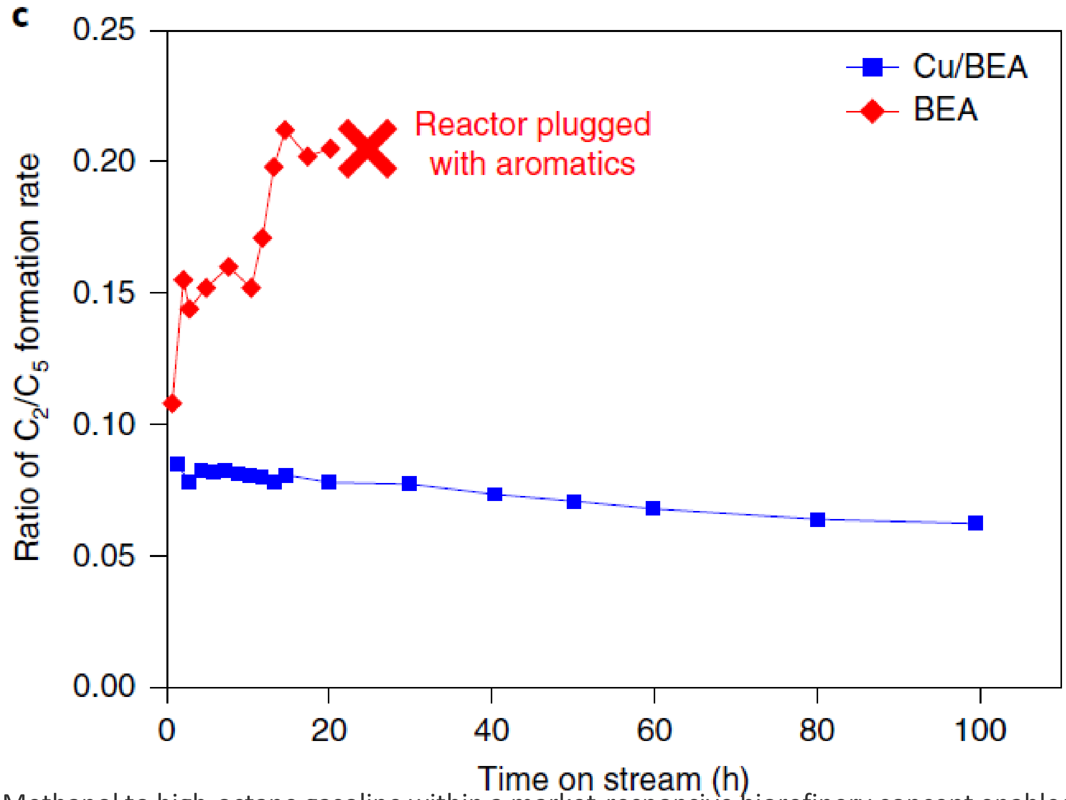
NREL Transforming ENERGY

Aromatic and Olefin Carbon Pools



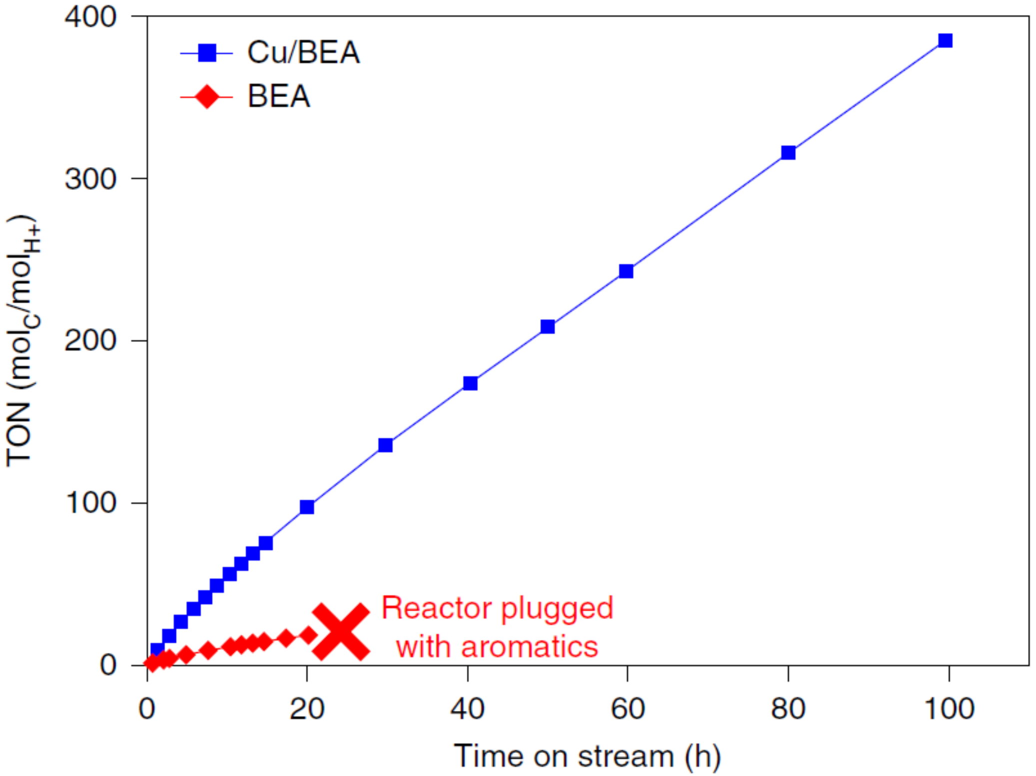
Ilias, S.; Bhan, A. Tuning the Selectivity of Methanol-to-Hydrocarbons Conversion on H-Zsm-5 by Co-Processing Olefin or Aromatic Compounds. J. Catal. 2012, 290, 186−192.

C2/C5 Ratio – Aromatic vs Olefin Pool



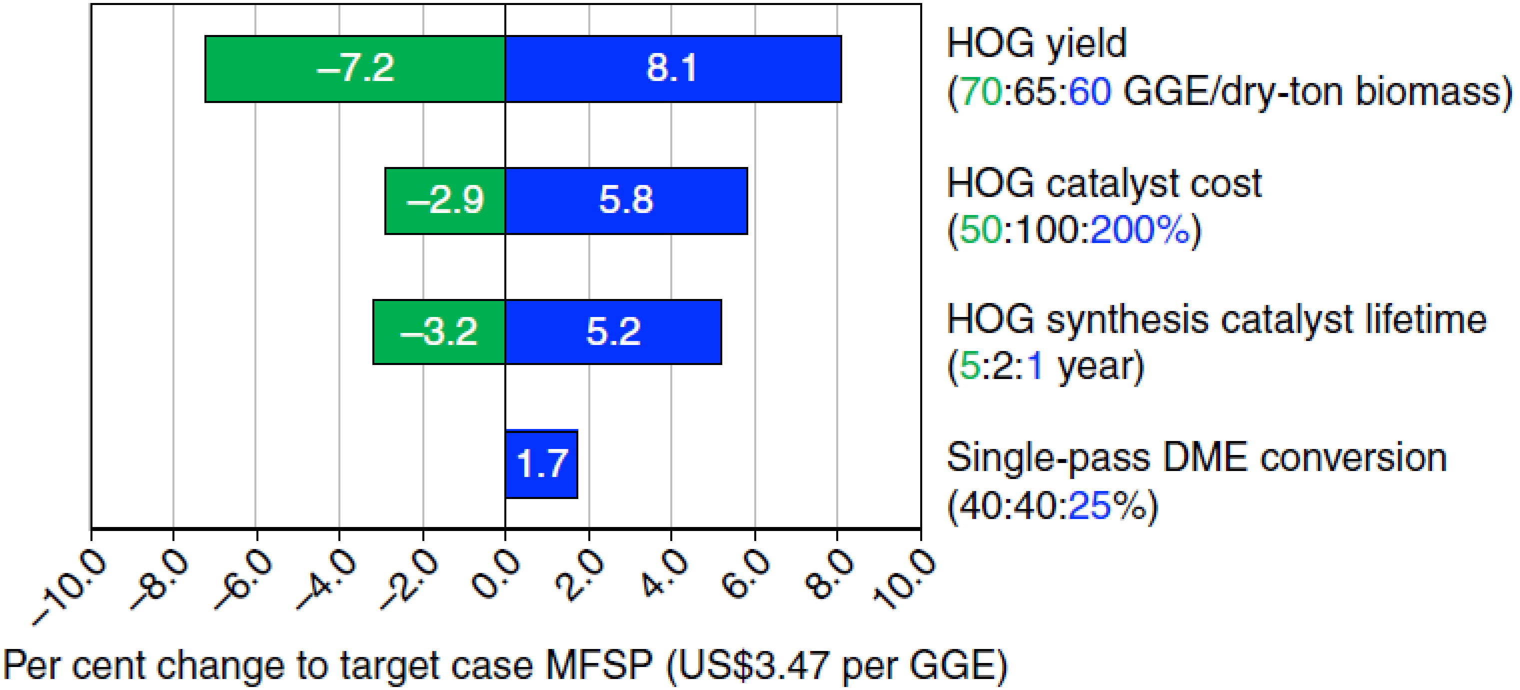
Ruddy, D. A. et al. Methanol to high-octane gasoline within a market-responsive biorefinery concept enabled by catalysis. J. Nat. Catalysis, 2019, 2, 632–640

DME Homologation TON vs TOS



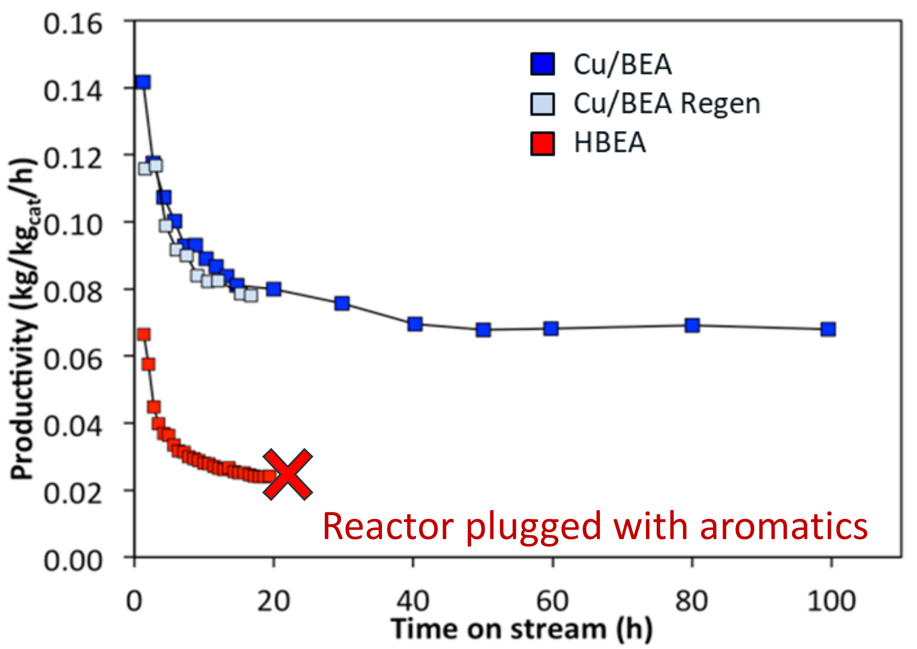
Ruddy, D. A. et al. Methanol to high-octane gasoline within a market-responsive biorefinery concept enabled by catalysis. J. Nat. Catalysis, 2019, 2, 632–640

HOG MFSP Sensitivity



Ruddy, D. A. et al. Methanol to high-octane gasoline within a market-responsive biorefinery concept enabled by catalysis. J. Nat. Catalysis, 2019, 2, 632–640

Metallic Cu/BEA improves productivity and lifetime



Ruddy, D.A., et al., Nature Catalysis, 2019.

US Pat # 9,714,387 B2 US Pat # 9,803,142 B1 US Pat # 9,796,931 B1