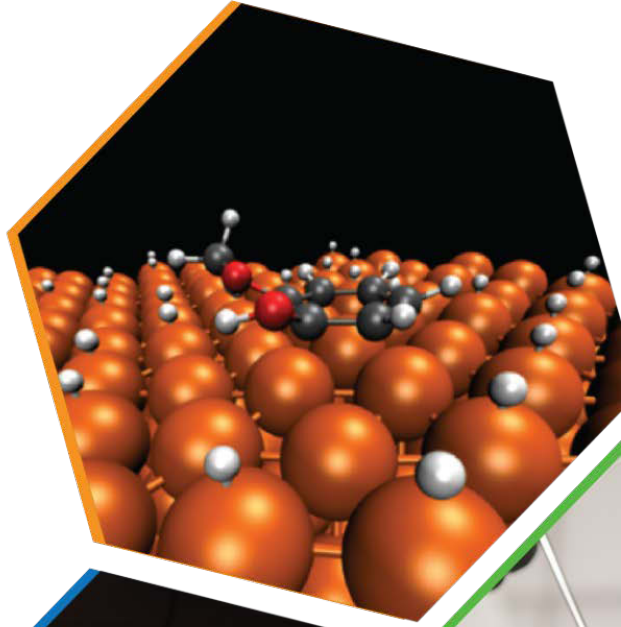
ChemCatBio
Chemical Catalysis for Bioenergy



A Full Spectrum of Characterization for Insight into Carbon Speciation and Removal on a Cu/BEA Catalyst During Renewable High-Octane Hydrocarbon Synthesis

Qiyuan Wu, National Renewable Energy Lab

ACS Spring 2021 National Meeting, April 7th 2021

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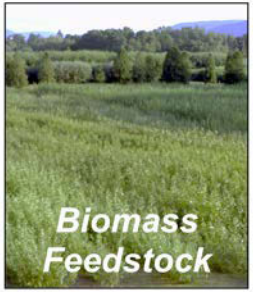
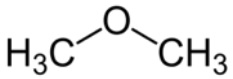
Overview – DME-to-HOG reaction

- DME homologation to high-octane gasoline



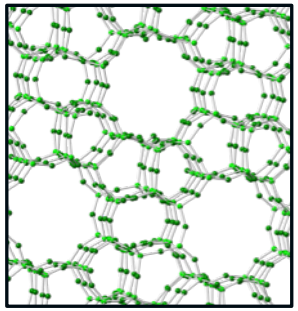
Dimethyl Ether (DME)



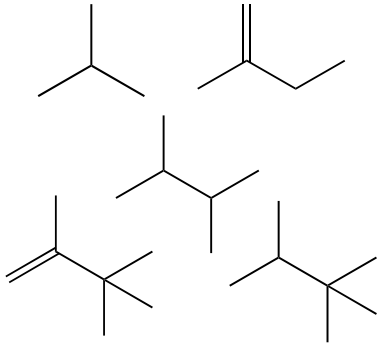
or Methanol CH_3OH

125-275 °C,
1-10 atm

Large-pore acidic zeolites (H-BEA)



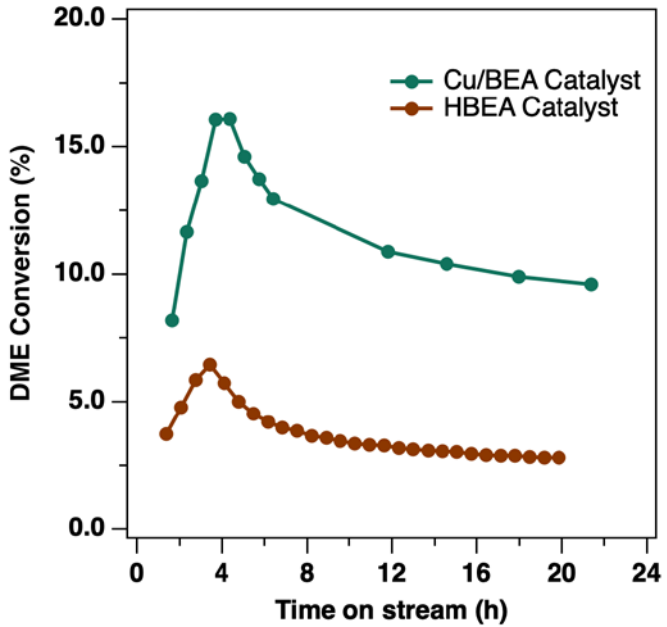
Branched Hydrocarbons (C_4-C_7)

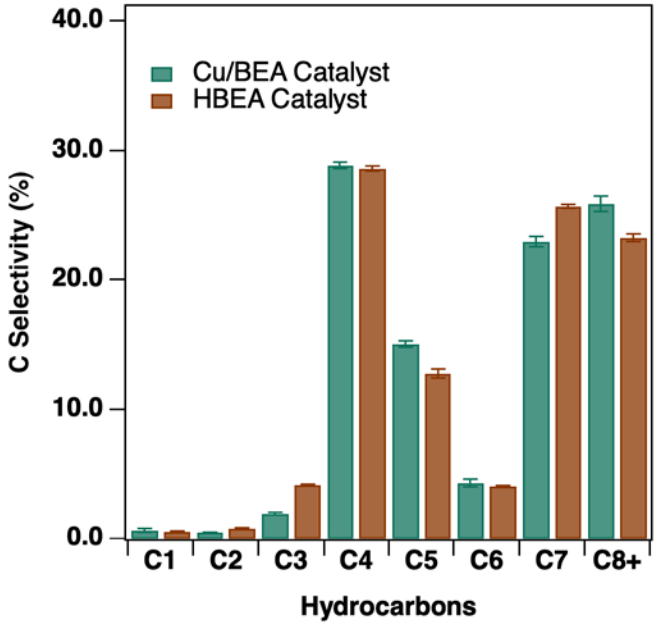


(Ahn et al., *Angew. Chem.*, 2009)
(Ahn et al., US Patent, 2009)
(Simonetti et al., *J. Catal.*, 2011)
(Simonetti et al., *ChemCatChem*, 2011)

Overview – DME-to-HOG reaction

- Addition of Cu significantly improves performance of BEA catalyst



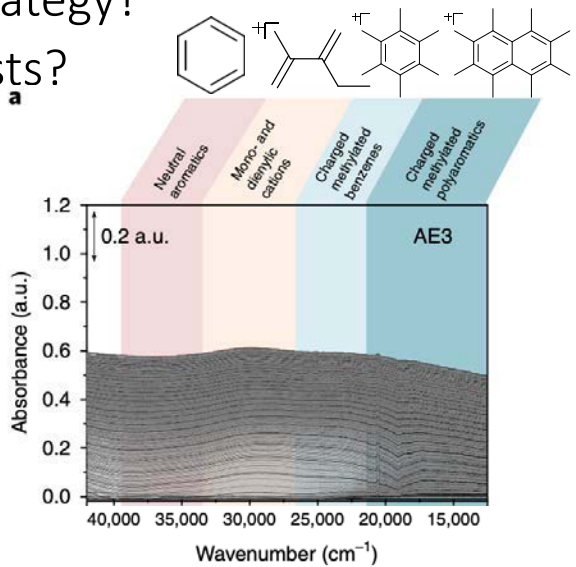


Project Overview – Regeneration strategy

- Need an efficient and effective regeneration procedure
  - Similar hydrocarbon pool chemistry in methanol-to-hydrocarbon
  - Different reaction condition
  - Different carbon species and regeneration strategy?
  - Difference between HBEA and Cu/BEA catalysts?

Reaction	Temperature	Pressure
MTH	300°C ~ 500°C	Up to 20 atm
DME-to-HOG	175°C ~ 225°C	1~10 atm

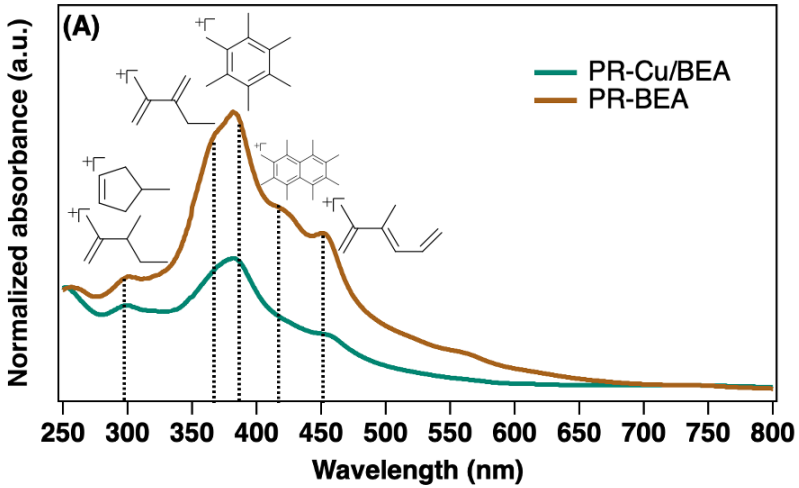
Typical regeneration temperature for MTH: > 600 °C

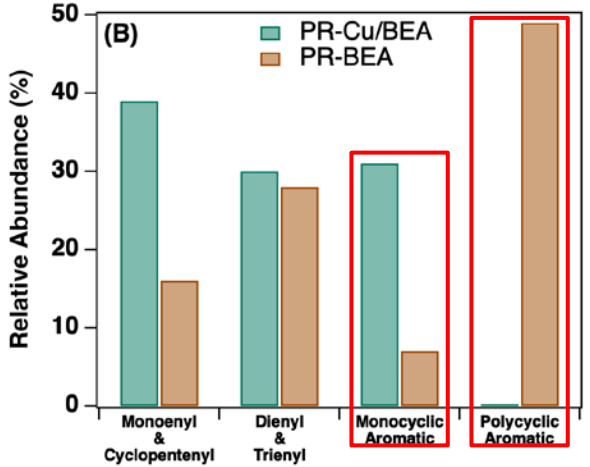


(Yarulina et al., *Nature Chemistry,* 2018)

Post-reaction catalysts analysis

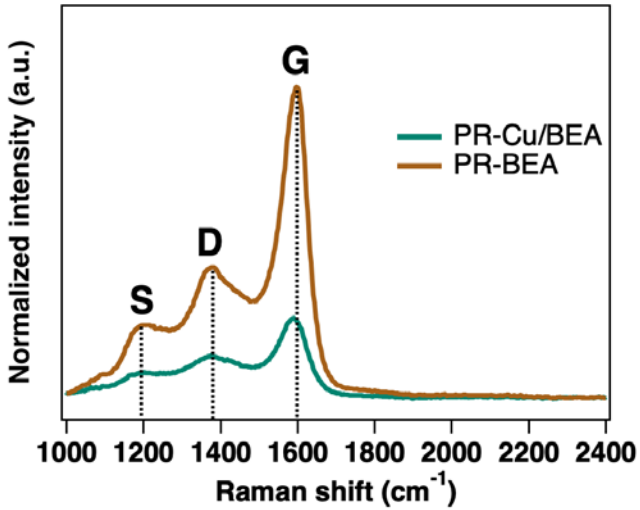
- Diffuse reflectance UV-Visible (DR-UV-Vis) spectroscopy
  - Sensitive to molecular hydrocarbon species
  - Similar to hydrocarbon species found in MTH
  - Significant lower relative abundance of aromatic in PR-Cu/BEA





Post-reaction catalysts analysis

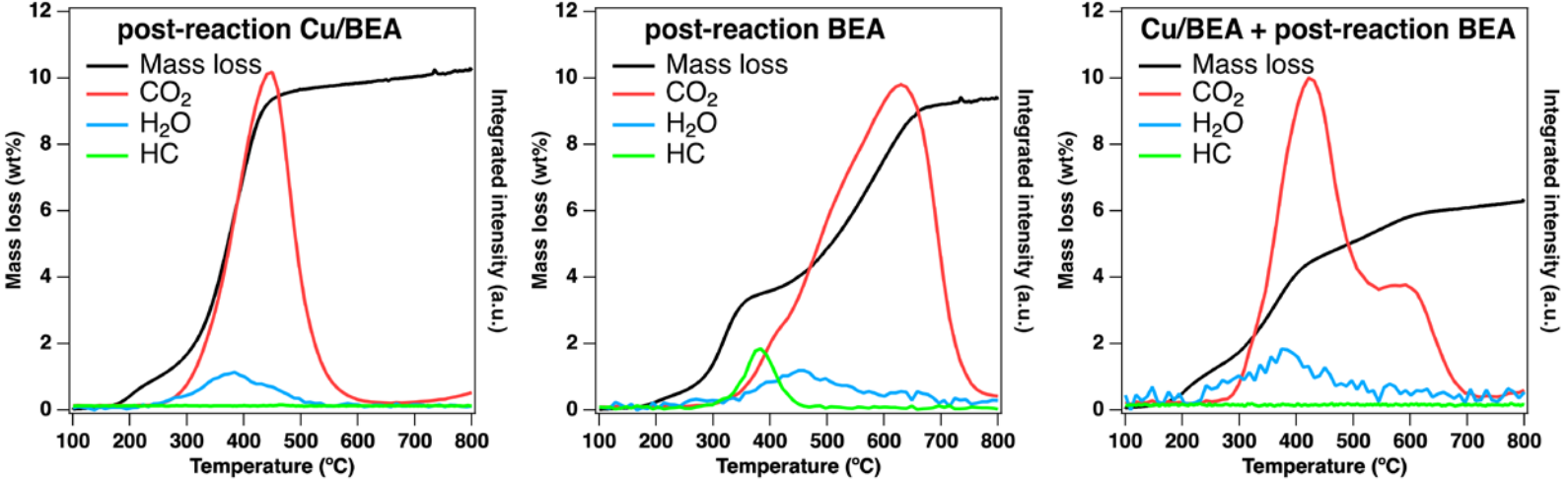
- Raman spectroscopy
  - Sensitive to extended carbon species
  - Presence of graphitic carbon
  - Graphitic carbon is more hydrogenated in PR-Cu/BEA



Catalyst	G position	D/G
Cu/BEA	1570 cm^{-1}	1.6
BEA	1590 cm^{-1}	1.2

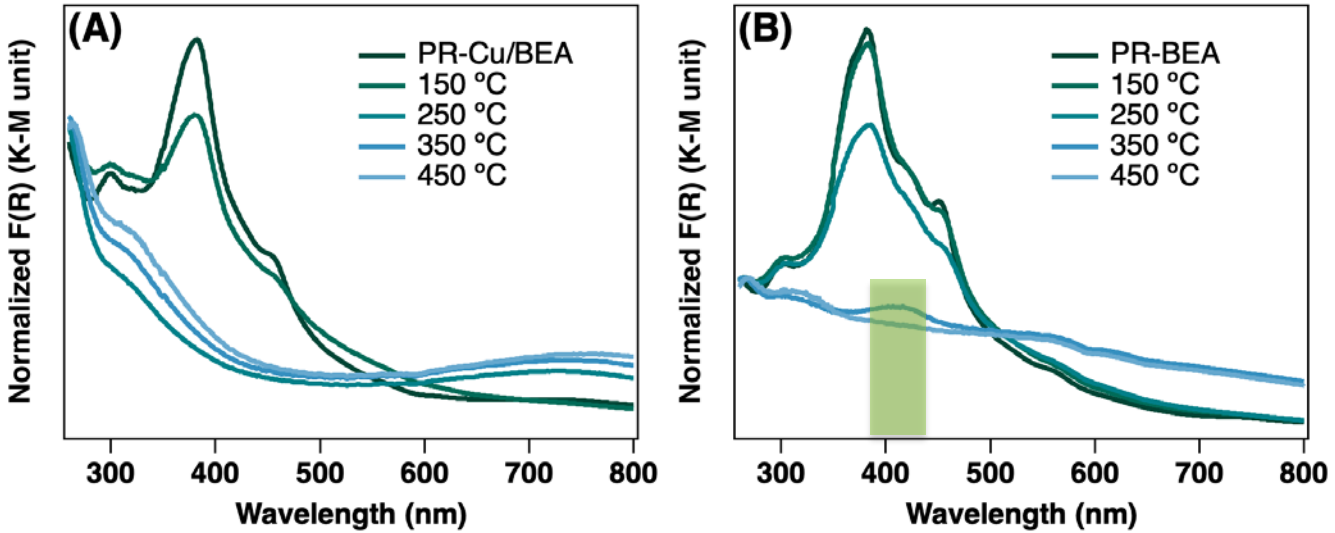
Post-reaction catalysts analysis

- Thermogravimetric – Fourier transform infrared (TG-FTIR) analysis
  - Oxidation of carbon species
  - IR spectra of oxidation products
  - Significantly lower temperature for carbon oxidation with presence of Cu



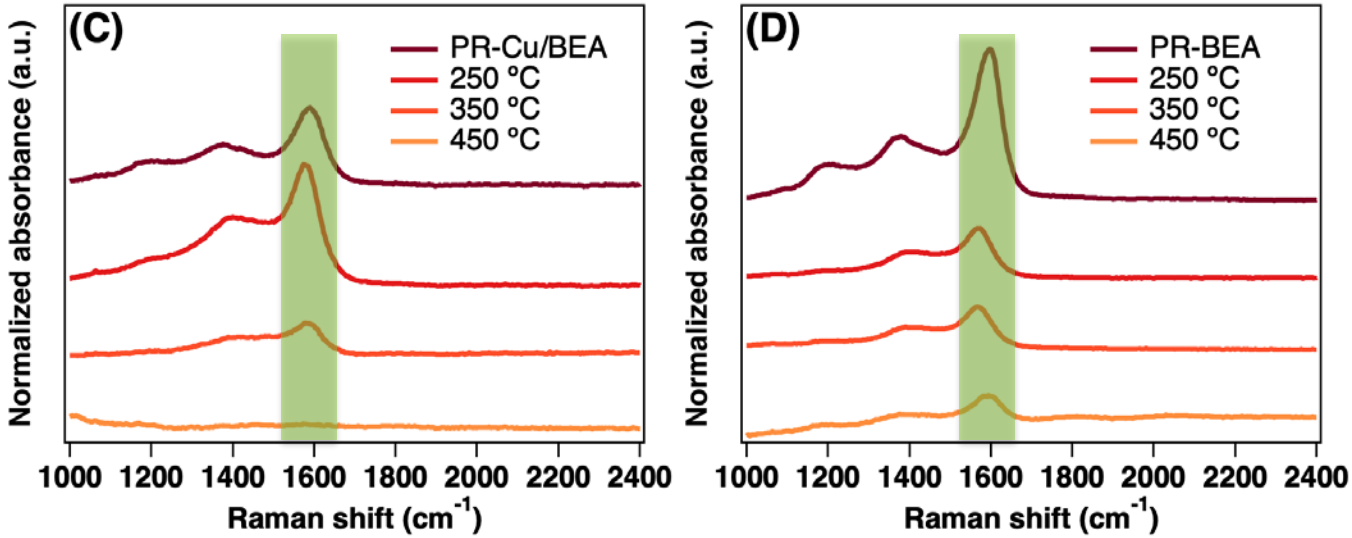
Post-reaction catalysts analysis

- In situ DR-UV-Vis spectroscopy
  - Oxidation of hydrocarbon species
  - ~ 250 °C to remove hydrocarbon over PR-Cu/BEA
  - > 350 °C needed for PR-BEA (for polycyclic aromatic)



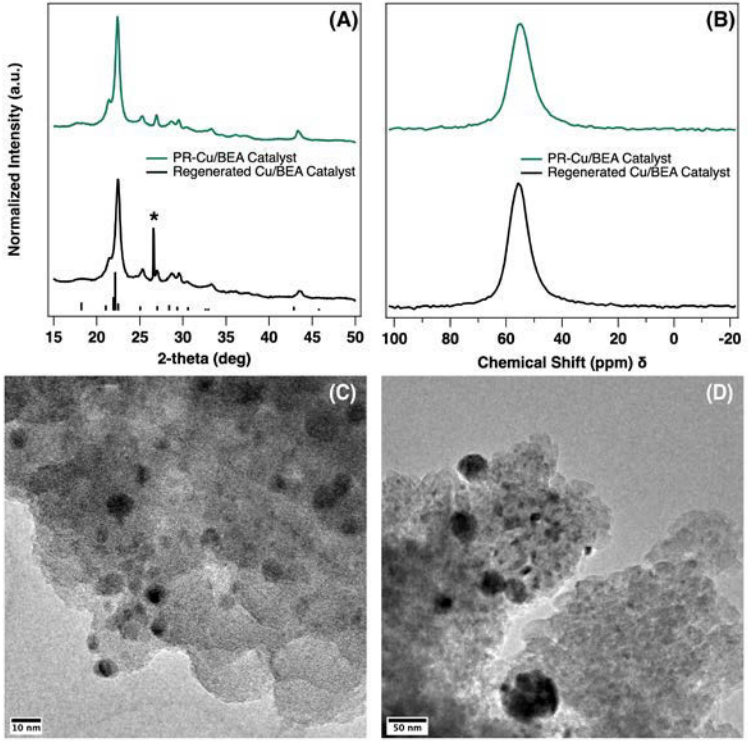
Post-reaction catalysts analysis

- In situ Raman spectroscopy
  - Oxidation of graphitic species
  - Lower temperature over PR-Cu/BEA as well
  - Cu activate oxygen



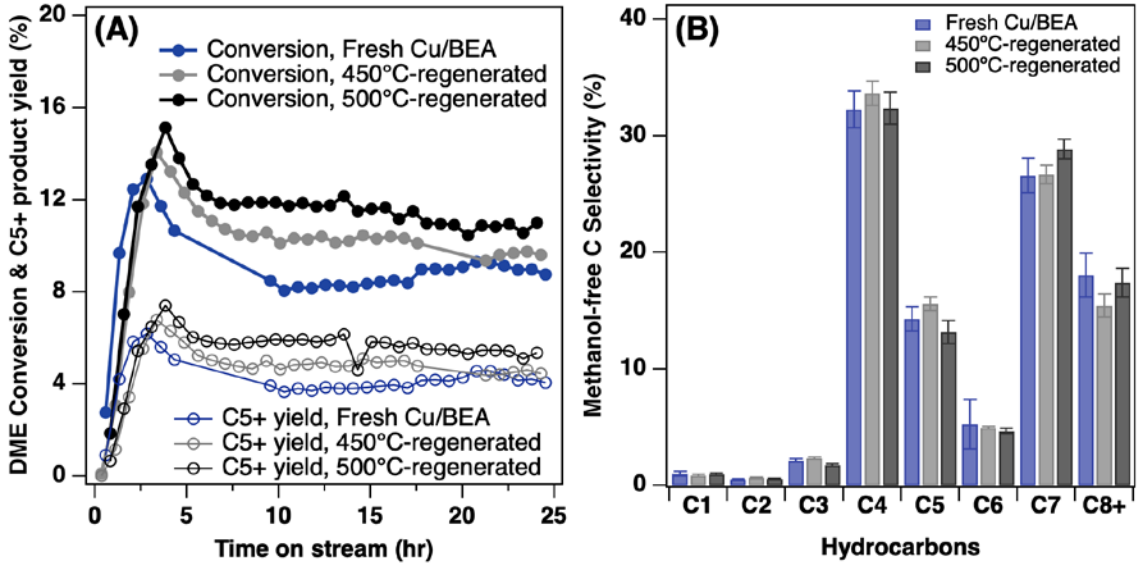
Cu/BEA catalyst regeneration

- Ex situ characterization
  - XRD, ^{27}Al MNR, and TEM to confirm structure



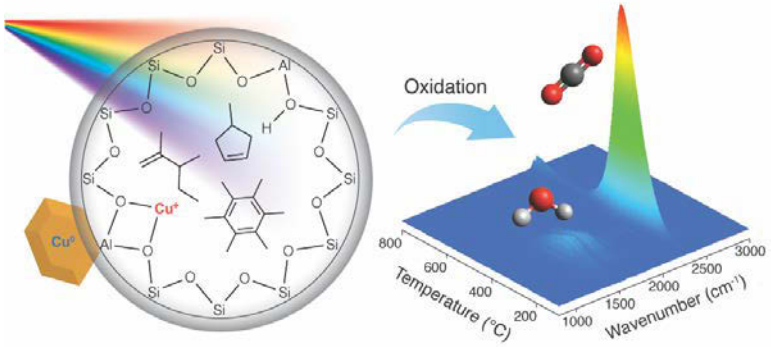
Cu/BEA catalyst regeneration

- Forced regeneration
  - 450 °C and 500 °C
  - Recover activity and selectivity



Summary

- Challenge
  - Determine speciation of carbon deposited on Cu/BEA catalyst during DME to high-octane gasoline reaction for catalyst regeneration
- Approach
  - Suite of (in situ) characterization technique: Cu activating oxygen
- Outcome
  - Developed an effective regeneration procedure that enabled full recovery of catalyst activity



Q. Wu, A. T. To, et al., *Appl. Catal. B,* 2021, 119925.
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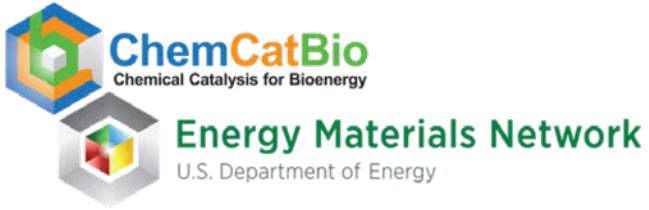

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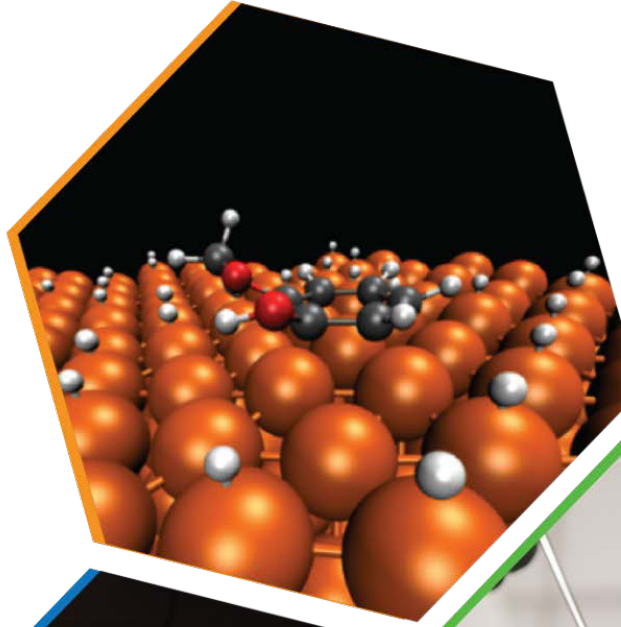

Thank you!

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