THE Ames Laboratory

Creating Materials & Energy Solutions

U.S. DEPARTMENT OF ENERGY

Fundamental Challenges and Opportunities in Complex Mixture Conversion

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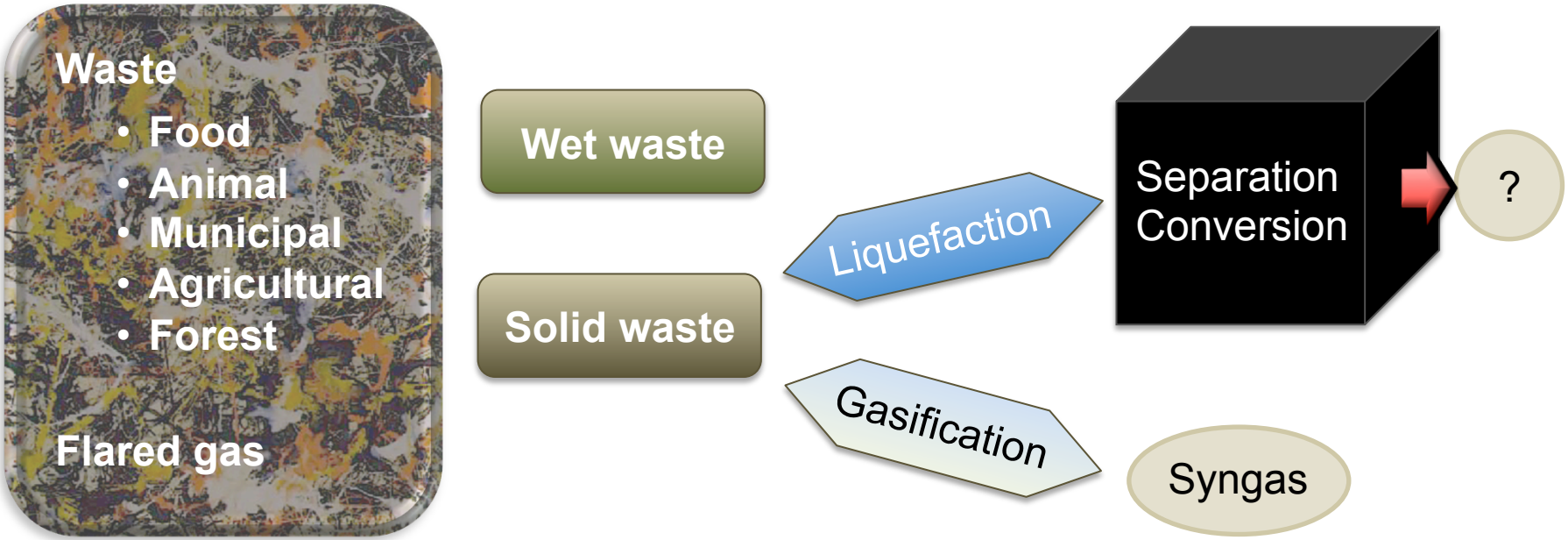
US DOE Ames Laboratory

More Specifically



THE OPPORTUNITIES

Waste

- **Lignocellulosics**
- **Polymers**
- **Protein degra-dation products**
- **Nitrates**
- **Pesticides**

Flared gas

Depolymerization

- Fermentation
- Pyrolysis
- Hydrocracking

- Sugars
- Phenolics
- Methyl sulfides
- N-heterocycles
- Ammonia
- Moderate to low deoxygeanted alkyls

Energy stored as chemical intermediates

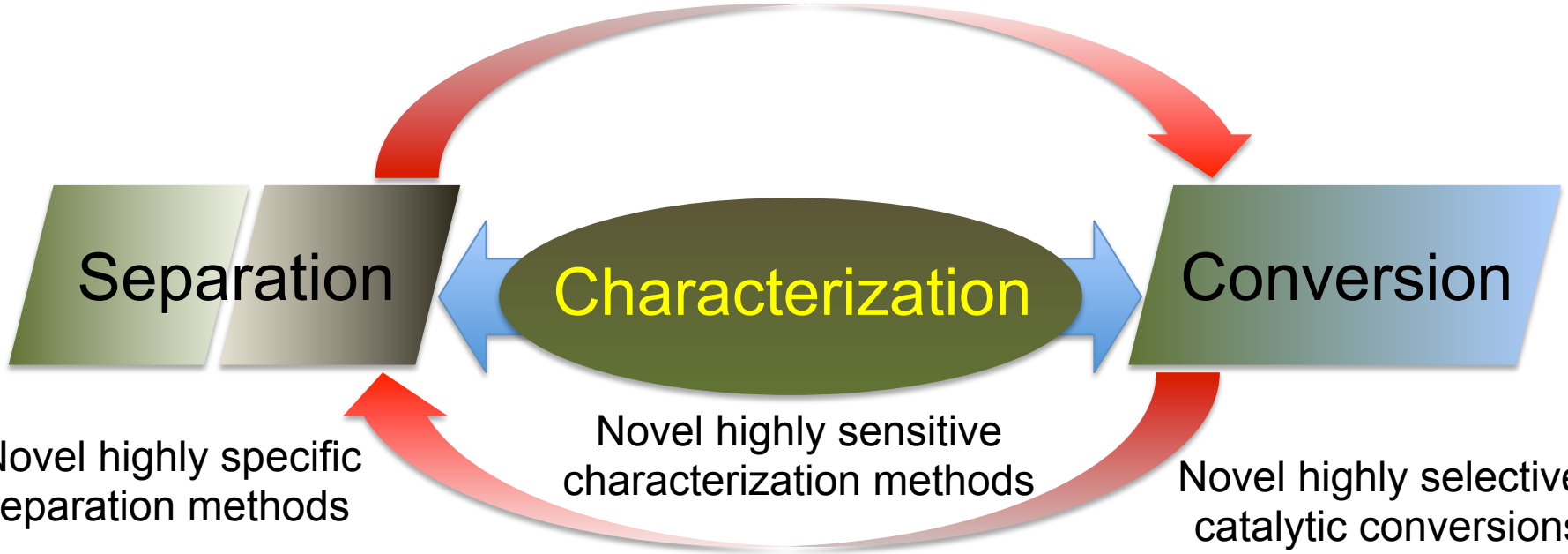
Precursors for

- Monomers
- Nutrients
- Lubricants
- Fuels

C-H activation

Target compounds to recover from food waste:
Galanakis, C.M. *Trends Food Sci. Technol.* **2012**, *26*, 68

Opportunities for Science



Separation pre-conversion

Separation during conversion

Separation post-conversion

Integration of separation and conversion?

Integrating Separation and Conversion

Issues with traditional fractionation methods

- High boiling compounds
- Decomposition prior to boiling
- Similar functionalities and MW

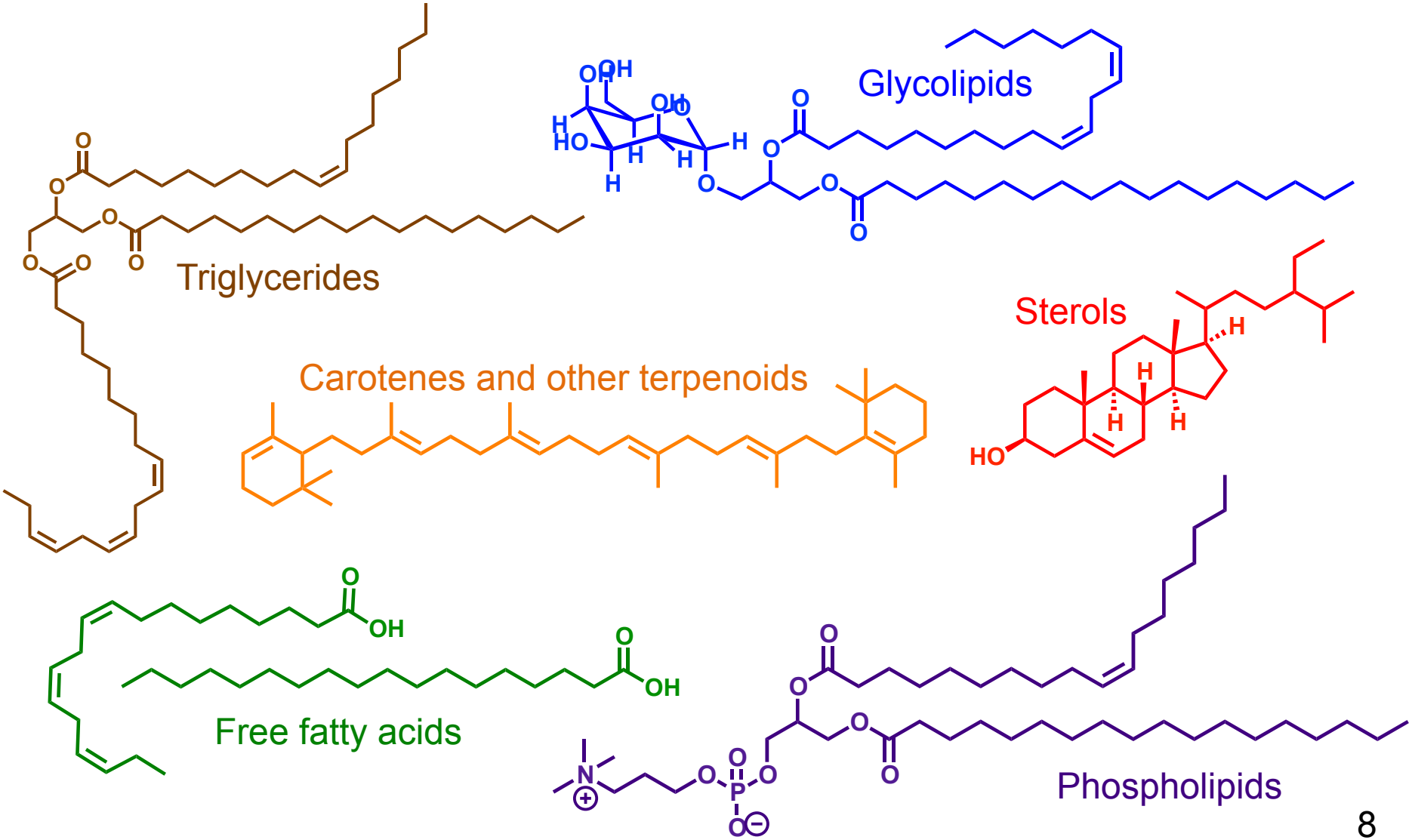
Molecular recognition methods may be useful for separation and conversion

- Recognition via specific intermolecular interactions:
  Functionality, charge distribution, molecular shape
- Molecular sieving

Integration of molecular recognition with catalysis as a tool to enhance separation and conversion efficiencies

Microalgal Oil: a Case of A Simple Complex Mixture

Microalgal Oil: a Case of A Simple Complex Mixture



Selective Sequestration of Oil Components

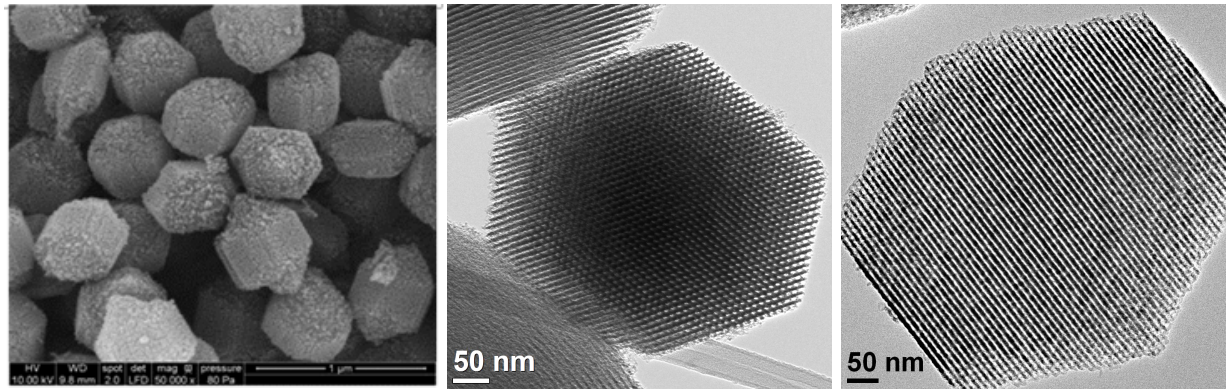
Solvent extraction
Fluorous phase extraction
Solid adsorbents

} Tailored for specificity
need multiple extractants...

Solid sorbents: large surface areas → Porous materials 1000s m^2/g

- Polymers, carbons, silicas, etc.

e.g. SBA-15 type Mesoporous Silica Nanoparticles

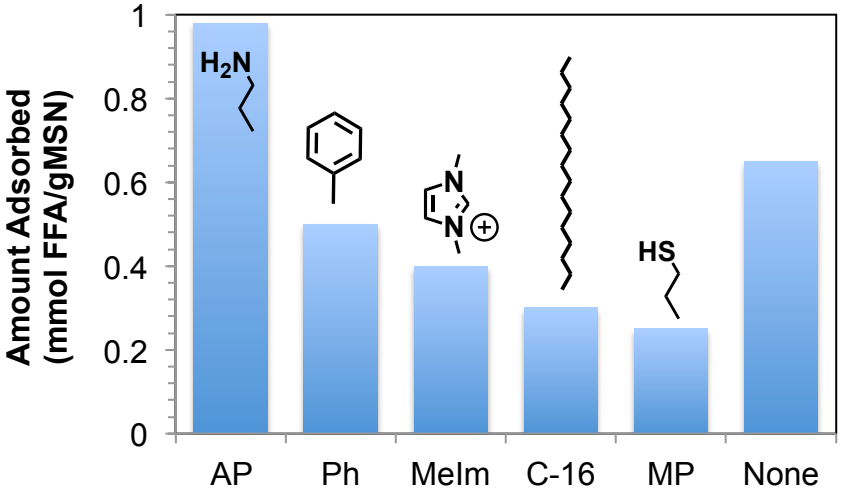


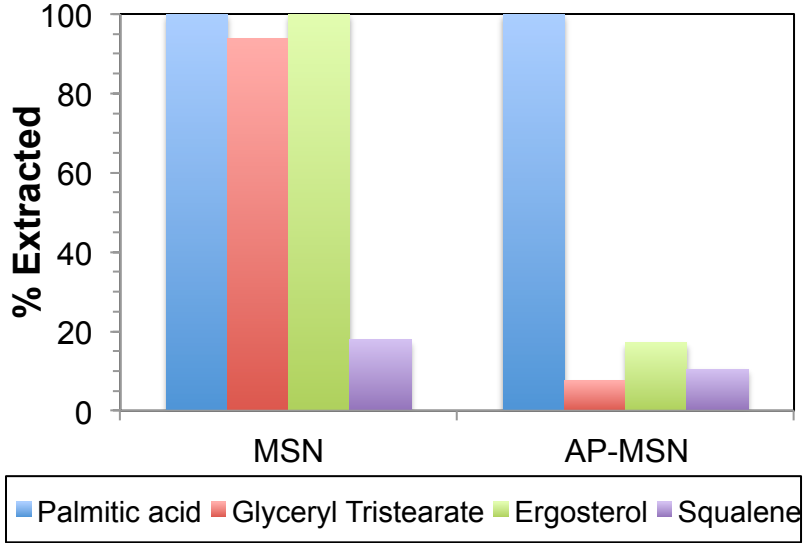
- Functionalization with recognition agents: organosilane chemistry

J. Mater. Chem., 20, 7924–7937, **2010**

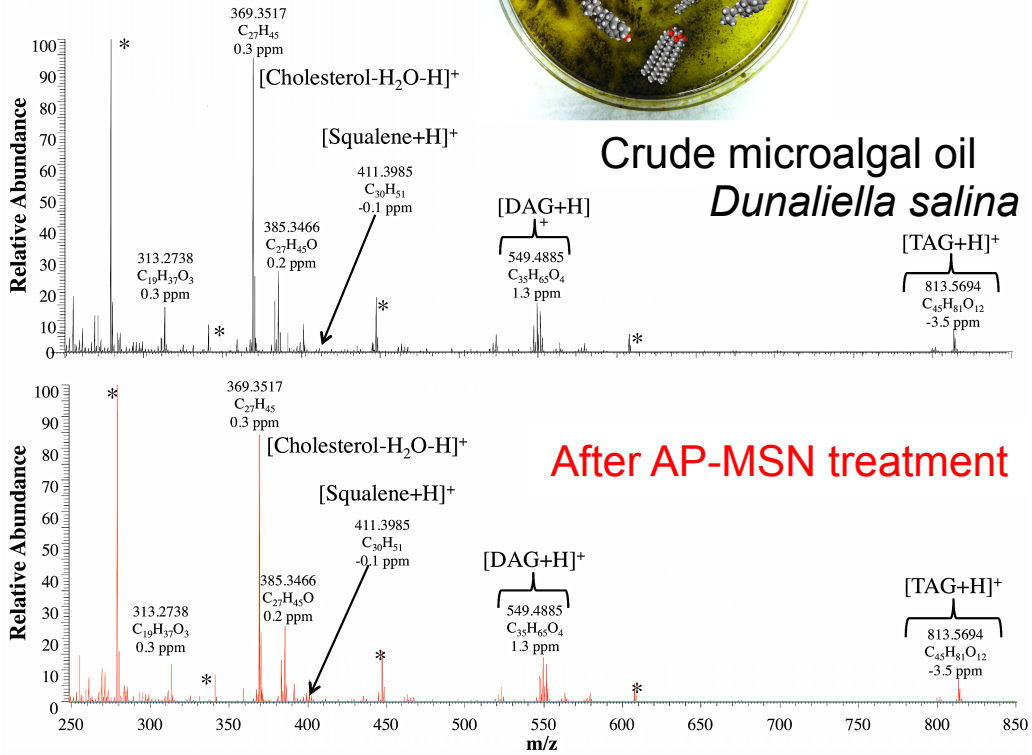
Selective Sequestration of Components via Chemical Interactions

Sequestration of FFA





APCI-HR-MS:



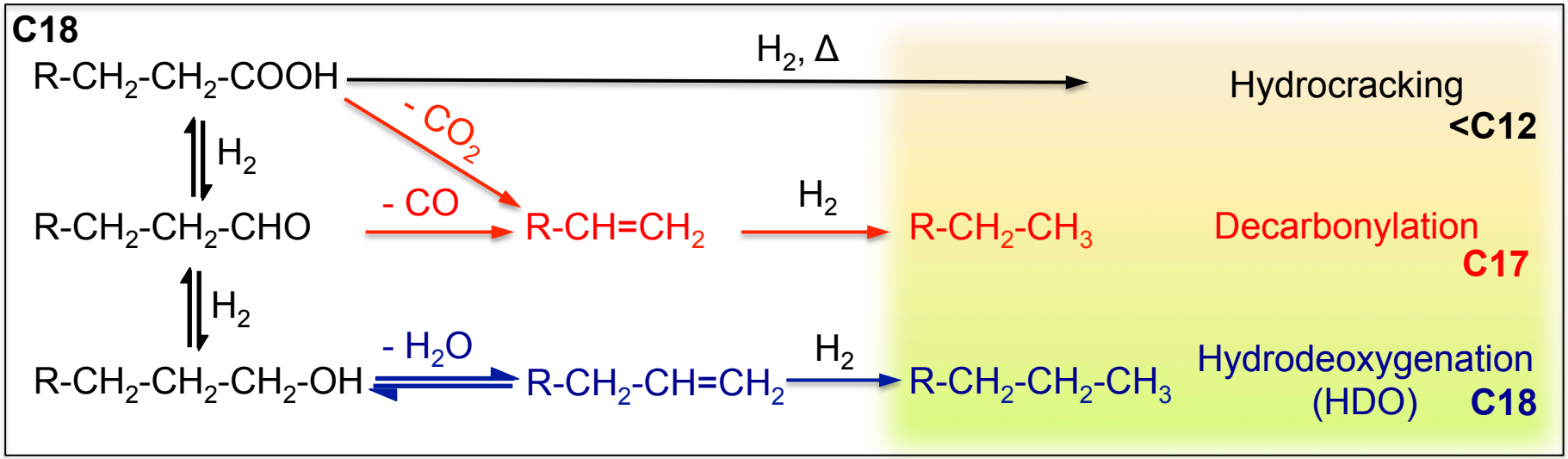
Crude microalgal oil
Dunaliella salina

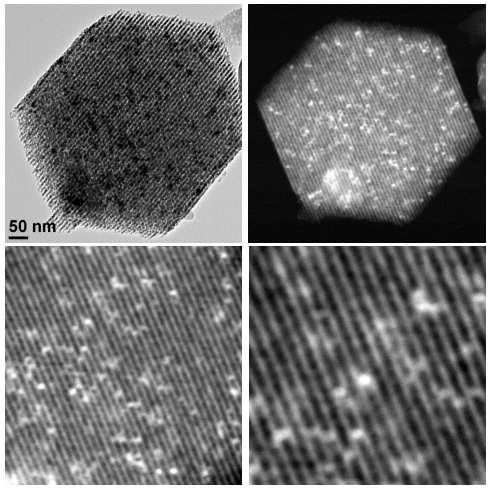
After AP-MSN treatment

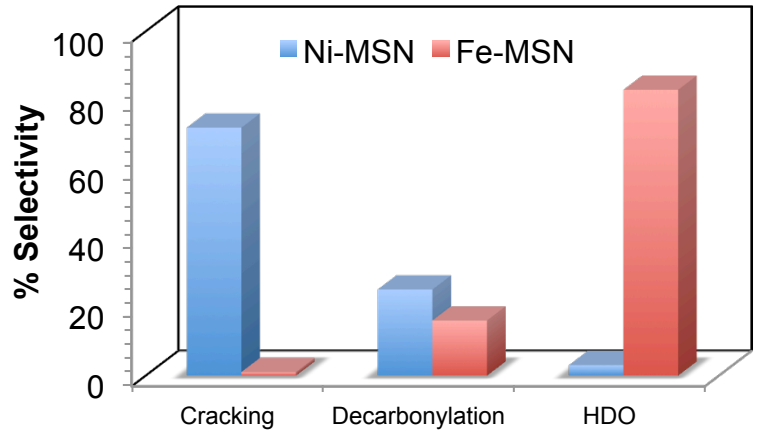
100 mg microalgal oil + 50 mg AP-MSN
FFA content: 11.5% → 0.70 %

ACS Appl. Mater. Interf., *4*, 1003-1009, **2012**

Hydrogenation of Fatty Acids

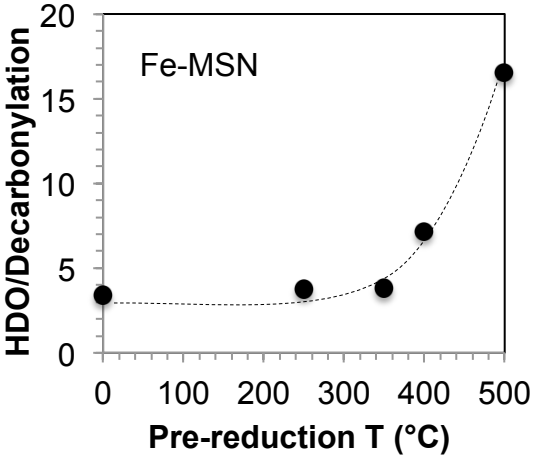






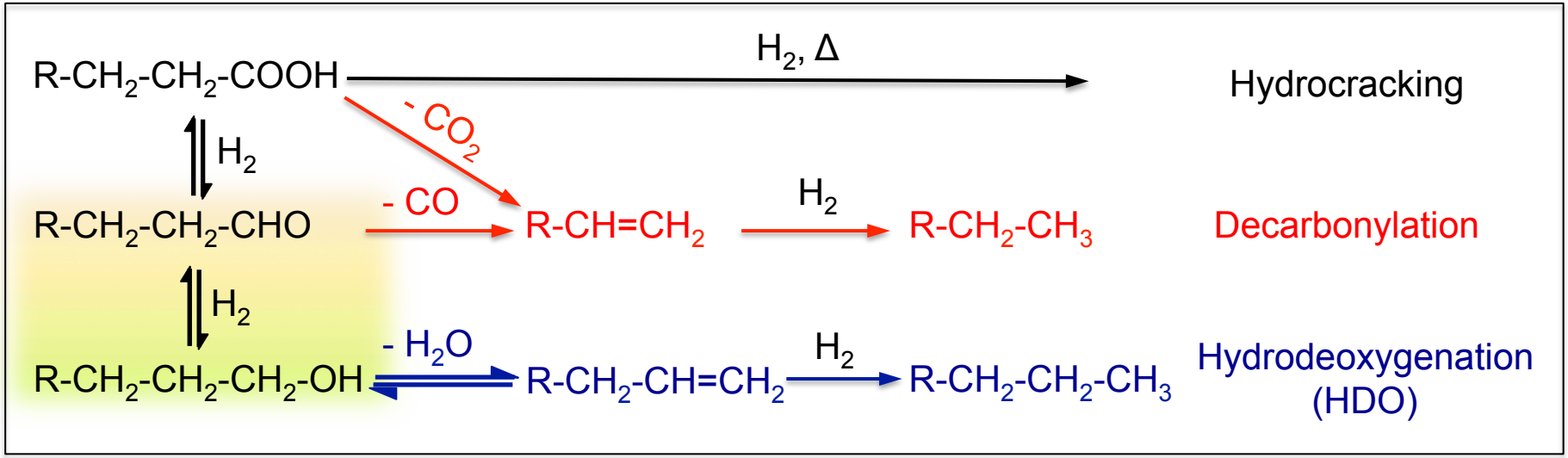
30 Bar H_2, 290 °C

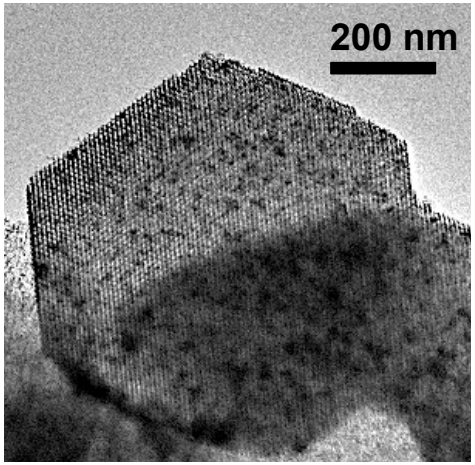
ACS Catal., *3*, 2750-2758, **2013**



J Catal., *314*, 142-148, **2014**

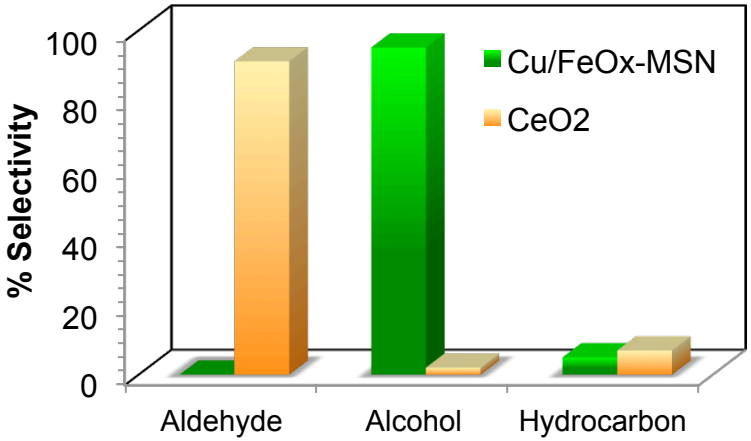
Additional Possibilities





CeO_2
250 °C, 30 bar H_2

Cu/FeOx-MSN
180 °C, 30 bar H_2



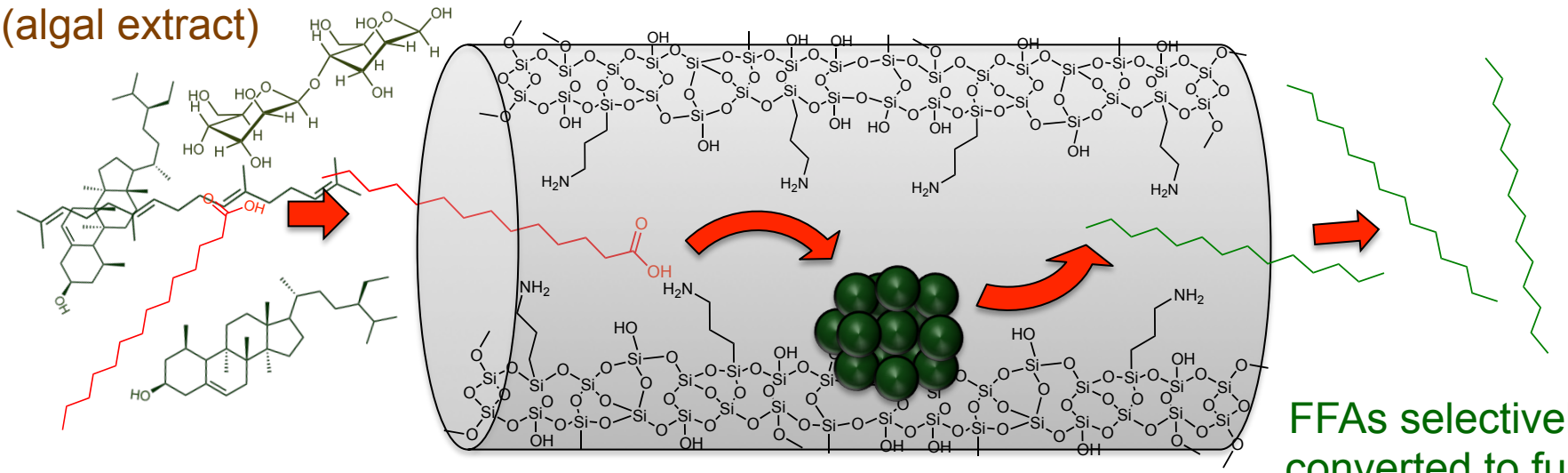
ACS Catal., *5*, 6719-6723, **2015**

Integrating Separation and Conversion

Two independent types of selectivity:

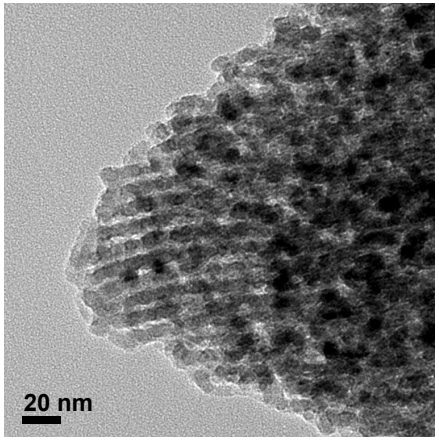
- Selective capture of FFA – Amines
- Selective conversion of FFA – Ni-MSN

Complex mixture (algal extract)



Input Selectivity

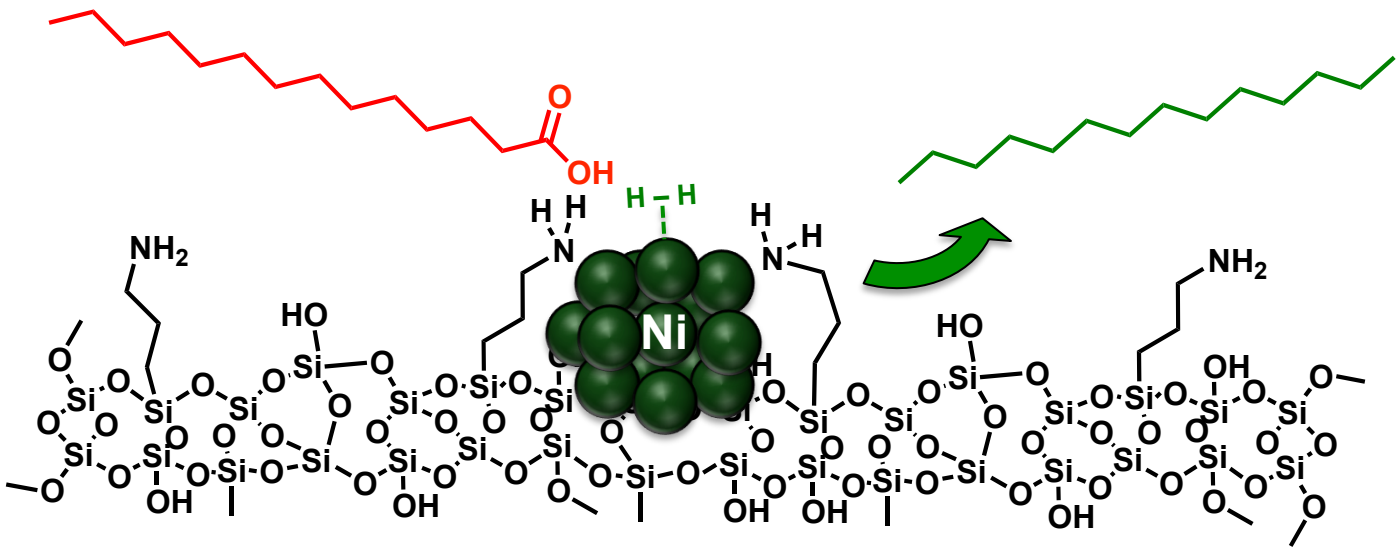
Sequestration: amines in pore

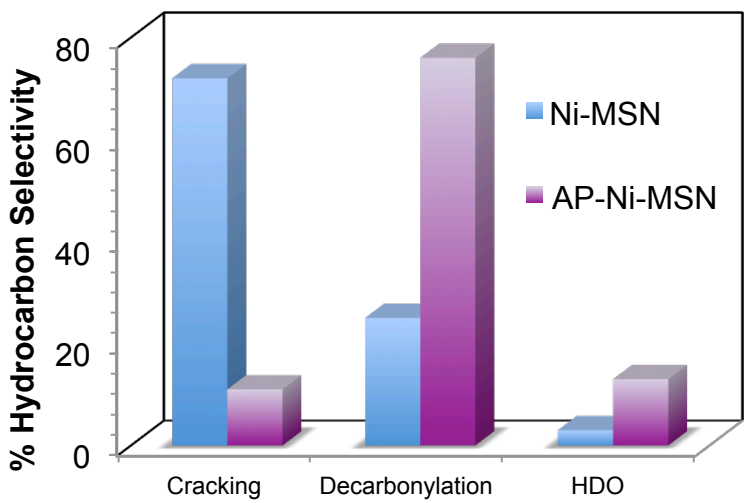


Output Selectivity

Reaction: Ni in pore

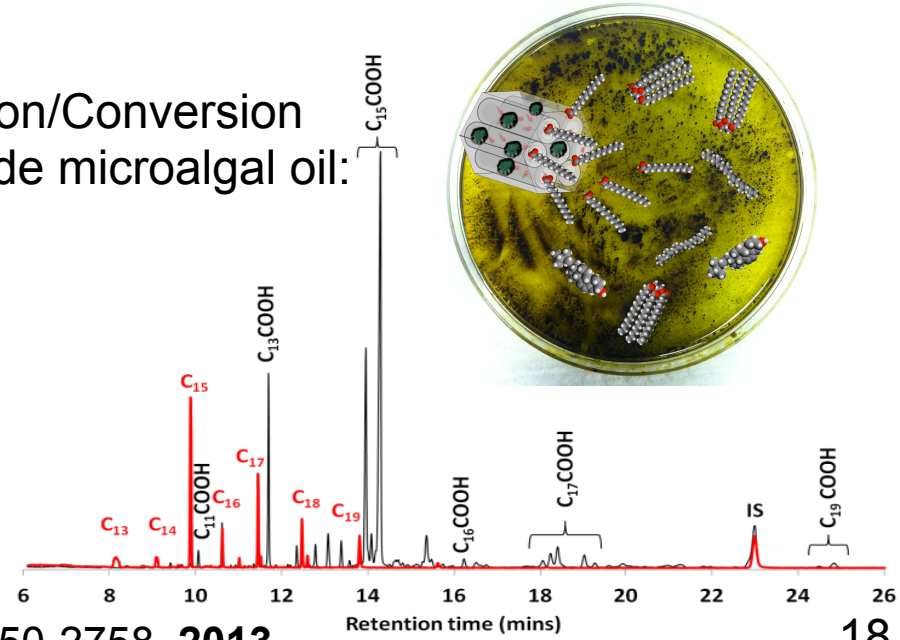
BUT… SYNERGISTIC EFFECTS





30 Bar H_2, 290 °C

Separation/Conversion from crude microalgal oil:



ACS Catal., *3*, 2750-2758, **2013**

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THANK YOU!