Introduction: energy sources and uses
The challenge of sustainable energy sources

New Materials: key to better devices (more stable, more efficient)

E.D. Cubuk, B. Malone, G. Tritsaris, B. Onat

Source: Report of Inter-Governmental Panel on Climate Change
S. Meng et al.

Artificial Nano Tree (based on QM simulations)

Cheng et al., JPCC (2008).
Motivation: Growing role of Chemical production in Industrial Energy demand

Global industrial energy use also is driven by the chemicals sector, where demand for energy is rising about 50 percent faster than overall energy demand.

Chemical companies use energy in two ways: as a fuel and as a feedstock to make plastics and other products essential to manufactured goods.

Need for catalysis research:
Chemical production relies on catalysis

- Catalysis for sustainable energy
- Catalysis for sustainable chemicals
- Optimization of existing industry
Reduction in energy cost using catalysis

- **Increase selectivity** — get the product you want with little or no waste

Example: Methanol oxidation on Ag or Au

\[
\text{CH}_3\text{O}-\text{C(H)=O} + 2 \text{H}_2\text{O} \rightarrow 3 \text{CH}_3\text{OH} + O_a \rightarrow \text{H}_2\text{C}=\text{O} + \text{CO}_2 + 2 \text{H}_2\text{O}
\]

Its all about *kinetics*!
Catalysis: Modification of kinetics via introducing intermediate steps

- Increase rate
- Lower operating temperature (save energy)
Rate-limiting step: H elimination from CH$_3$O

Electron distribution leads to reaction of negatively polarized species with positively charged one.

**Prediction:** Any molecule with electron-deficient carbon should react with OCH$_3$ on O/Au surface (e.g. CO or NR$_2$)
EFRC Participants:

Harvard:
  C.M Friend, E. Kaxiras, D. Bell, J. Hoffman, R. Madix

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BNL: Y. Zhu
EXA Corp: S. Melcionna

Goal: Develop design principles for increasing selectivity and lower operation temperatures to reduce energy expenditure
The Office of Basic Energy Sciences in the U.S. Department of Energy’s Office of Science established the Energy Frontier Research Center (EFRC) program, to accelerate such transformative discovery, combining the talents and creativity of our national scientific workforce with a powerful new generation of tools for penetrating, understanding, and manipulating matter on the atomic and molecular scales.
EFRC mission statement:
To develop a fundamental understanding of how to design and use novel mesoporous catalyst architectures for sustainable conversion and production of platform chemicals through selective oxidation and selective hydrogenation

RESEARCH PLAN
Principles for designing catalytic processes that will reduce energy consumption in producing chemical production will be constructed using advanced experiment and theory. Porous catalyst architectures will be studied under a wide range of conditions in order to optimize production of most desirable products.
Nanoporous Au: Dilute Ag/Au alloys exploit the ability of Ag to dissociate O\textsubscript{2}

Nanoporous Au Microspheres
1-3 at\% Ag (EDS)

Nanoporous Au Ingots
1-3 at\% Ag (EDS)
Environmental TEM shows dynamic nature of catalyst: CH$_3$OH + O$_2$ on npAu

CH$_3$OH (0.05 torr) + O$_2$ (0.1 Torr)

Vacuum, 1 hr.

O$_2$ (0.1 torr)

CH$_3$OH (0.05 torr) + O$_2$ (0.1 Torr)
The role of theory: “Multiscale modeling of complex chemical systems”

Macroscopic → Mesoscopic → Microscopic

Prof. Sauro Succi
Applied Computation 274:
Computational modeling of fluids and soft matter
Methoxy splitting on TiO$_2$ surface

- Formaldehyde was photochemically produced from methoxy on TiO$_2$ (110) surface

\[
\text{CH}_3\text{O}^{(a)} + \text{O}^{(a/br)} + h^+ \rightarrow \text{H}_2\text{CO}^{(a)} + \text{OH}^{(a/br)}
\]

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G. Kolesov
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Example: ozone photolysis

• Excitation HOMO to LUMO: slow dissociation

• Excitation HOMO to LUMO+1: quick dissociation

Wrong excitation (visible light)
Right excitation (UV light)
2\textsuperscript{nd} excited state trajectory

- Movie: o3split.mov
TDDFT trajectory:

Electron

Hole

0.0 fs

0.0 fs

O-H 1.76
C-H 1.19

O-H 1.76
C-H 1.19
Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC)

- Understanding kinetics
- Building innovative catalytic architectures
- Improved reaction selectivity

- Sustainable catalytic systems
- Efficient and benign by-products
- Decreased fuel consumption

Selective oxidation and hydrogenation reactions
$10^5$ torr $\rightarrow$ 1 atm

Multi-scale computational modeling
Atomistic $\rightarrow$ Macroscopic