

Methane activation: Inspiration from Nature

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**ARPA-E ELECTROCHEMICAL APPROACHES TO
MODULAR POWER GENERATION WORKSHOP**

June 6-7, 2013

Crowne Plaza Avenue Hotel

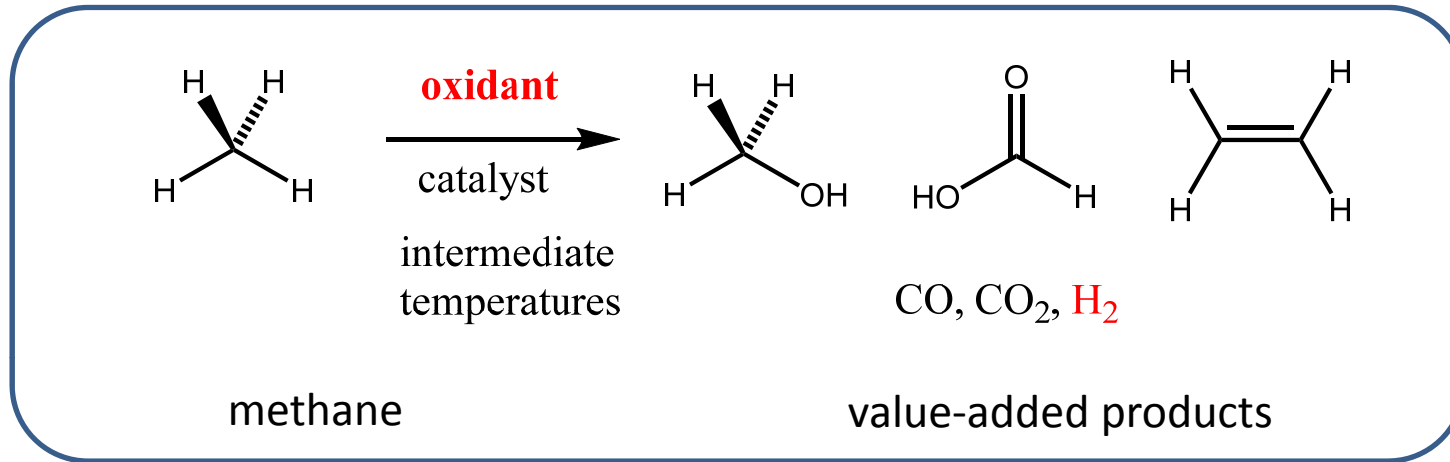
160 E. Huron St.

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arpa·e
CHANGING WHAT'S POSSIBLE



a grand challenge for catalysis



large domestic reserves

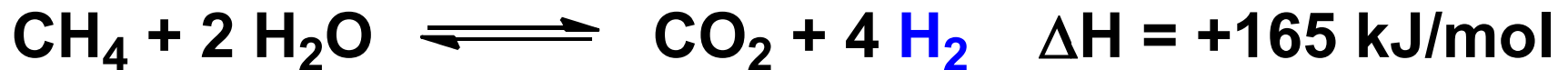
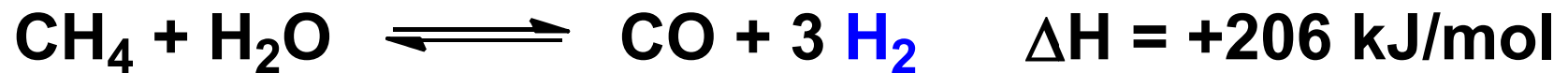
steam reforming energy intensive

not ideal for transportation/portable devices

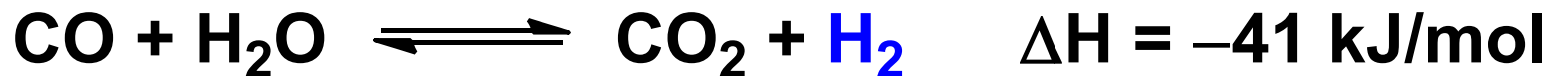
How can we achieve the selective partial oxidation of methane?

thermodynamics of the steam-methane reforming process

Hydrogen formation via methane reforming is highly endothermic



H₂ formation via water-gas shift is slightly exothermic



at intermediate temperature: coking challenge with Nickel

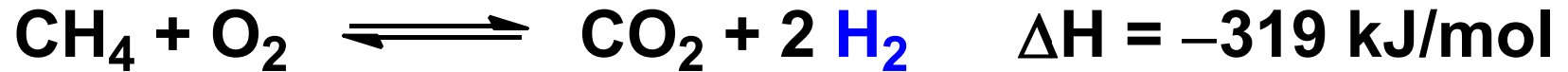
many homogenous catalysts can activate C-H bonds

PERIODIC TABLE OF THE ELEMENTS

1	H																	He	
2	Li	Be											B	C	N	O	F	Ne	
3	Na	Mg										Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	Cs	Ba			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra			Rf	Db	Sg	Bh	Hs	Mt	Ds	Rn	Cn	Uut	Uuq	Uup	Uuh	Uuq	Uuo
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Pioneering studies by Bergman, Bercaw, Graham, Jones, Crabtree, Periana, and more
Recent studies by Hartwig, Smith, Mendiola, Goldberg, Sanford, White, Yu, and more

reforming with molecular oxygen

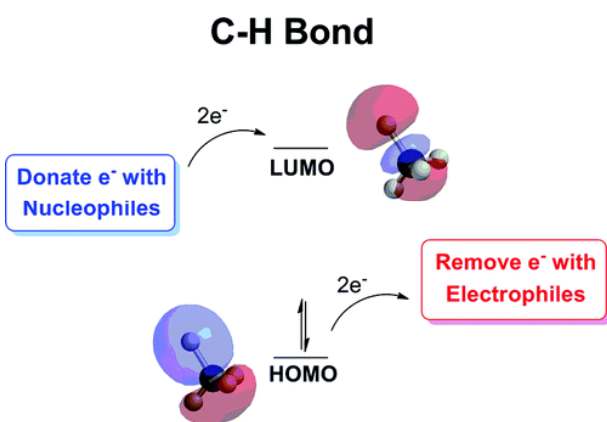


Oxygen renders process highly exothermic

Could the right system result in partial oxidation?

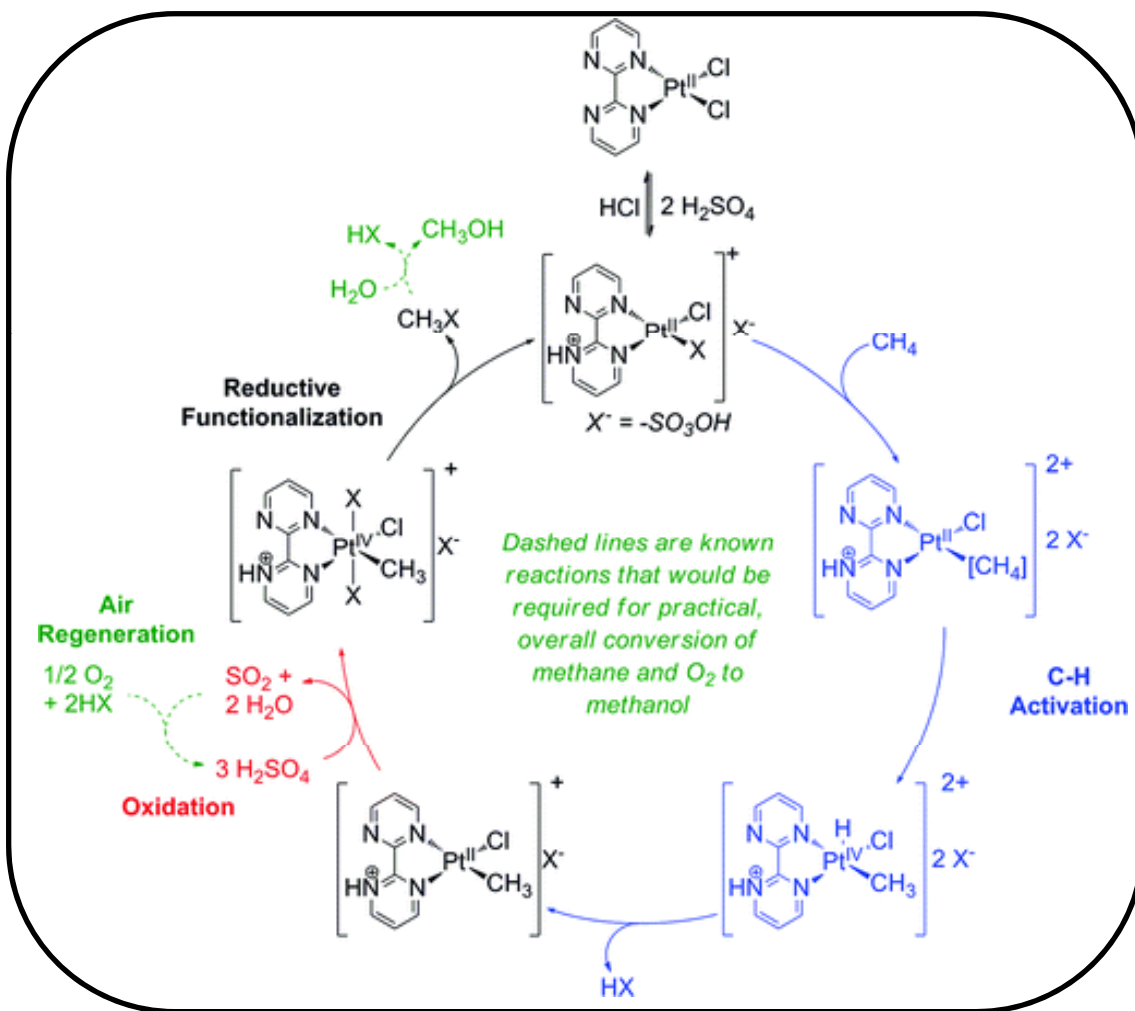
methane to methanesulfonic acid

Periana and coworkers, *Accounts of Chemical Research*, 2012



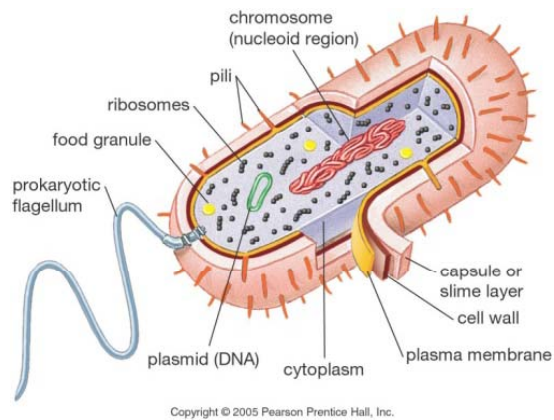
(1) activate catalyst

(2) protect product

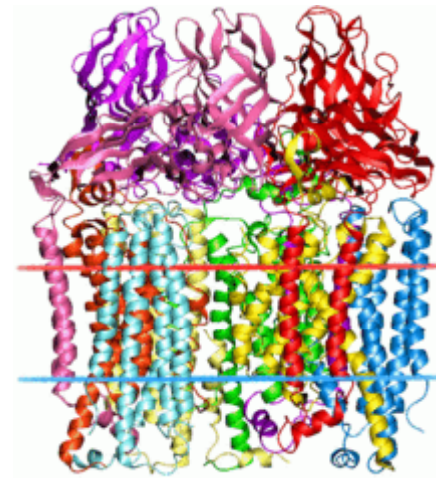


highly acidic medium essential, but not yet practical

lessons from methanotrophs



bacteria that can metabolize methane



methane monooxygenase (MMO)

Can we design a catalytic system inspired by MMO?

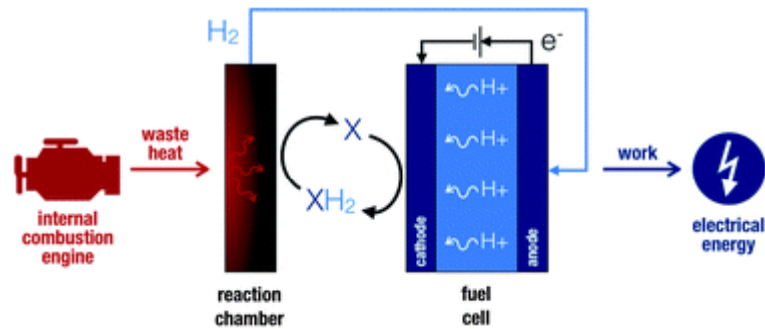
Ideas for selective methane activation



Design of novel catalysts, oxidants, systems needed

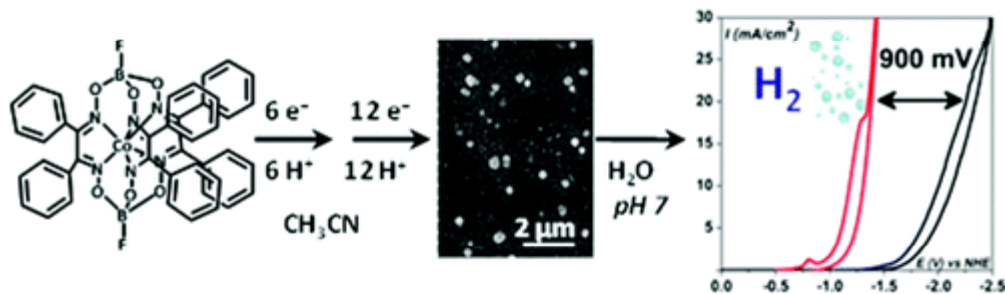
why not IT fuel cells?

fuel cell coupled to an internal combustion engine



By Phillip Jessop

renewable sources of hydrogen or other fuels in the future



By Jean-Michelle Saveant

special thanks

John Lemmon
Jonathan Burbaum
Hannah Ray

I-Hon Chen
Qing-An Chen
Stephen Murphy
Nathan Oldenhuis
Kevin Kou
Daniel Kim
Kyle Schenthal