Methane activation:
Inspiration from Nature

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a grand challenge for catalysis

- Oxidant
- Catalyst
- Intermediate temperatures

methane → value-added products

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

CH$_4$ + H$_2$O $\leftrightarrow$ CO + 3 H$_2$ \hspace{1cm} \Delta H = +206 \text{ kJ/mol}

CH$_4$ + 2 H$_2$O $\leftrightarrow$ CO$_2$ + 4 H$_2$ \hspace{1cm} \Delta H = +165 \text{ kJ/mol}

H$_2$ formation via water-gas shift is slightly exothermic

CO + H$_2$O $\leftrightarrow$ CO$_2$ + H$_2$ \hspace{1cm} \Delta H = -41 \text{ kJ/mol}

at intermediate temperature: coking challenge with Nickel
many homogenous catalysts can activate C-H bonds

Pioneering studies by Bergman, Bercaw, Graham, Jones, Crabtree, Periana, and more
Recent studies by Hartwig, Smith, Mindiola, Goldberg, Sanford, White, Yu, and more
reforming with molecular oxygen

\[ \text{CH}_4 + \text{O}_2 \rightleftharpoons \text{CO}_2 + 2 \text{H}_2 \quad \Delta H = -319 \text{ kJ/mol} \]

\[ 2 \text{CH}_4 + \text{O}_2 \rightleftharpoons 2 \text{CO} + 4 \text{H}_2 \quad \Delta H = -71 \text{ kJ/mol} \]

*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
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