Energy Source Chemistry

Introduction

The picture was taken in 1970s. An average American Family is surrounded by the barrels of oil they consume annually. Now this consumption is about 40% higher. The world’s growing thirst for oil amounts to almost 1000 barrels a second, which means about 2 liters a day per person. We are facing the severe energy problems now. -How long can we keep running this road? -Can scientists find an energy source capable of replacing fossil fuel? -Can chemistry help in solving the energy problem?
The Chemistry in "Novel" Energy Source:
1. H₂ Storage
2. Methane Oxidation
3. Solar Energy

ACIEE, 2007, 46,52

1. H₂ Storage

Hydrogen is a promising energy carrier in future energy systems. However, storage of hydrogen is a substantial challenge.

<table>
<thead>
<tr>
<th>Liquid hydrogen</th>
<th>Cryo-adsorption</th>
<th>Interstitial metal hydride</th>
<th>Compressed hydrogen</th>
<th>Alcamet</th>
<th>Sub-like metal hydride</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH2</td>
<td>Activated carbon</td>
<td>Liquid Phase Comp./-metal,</td>
<td>CGH₂</td>
<td>NaH₂</td>
<td>MgH₂</td>
<td>H₂O</td>
</tr>
<tr>
<td>100 mat.wt%</td>
<td>6.5 mat.wt%</td>
<td>Liquid Phase Comp./metal,</td>
<td>100 mat.wt%</td>
<td>7.5 mat.wt%</td>
<td>11 mat.wt%</td>
<td></td>
</tr>
</tbody>
</table>

Operating temperature:
-253°C > 200°C 0 ~ 30°C 25°C 70 ~ 170°C 330°C > 300°C

Corresponding energy to release hydrogen in MJ per kg H₂:
0.45 3.5 15 n/a 23 37 142

Physical storage:
1. high-pressure and cryogenic-liquid storage
2. adsorption storage on high-surface-area adsorbents

Chemical storage:
1. hydride
2. hydrogenation/dehydrogenation of liquid hydrogen carrier
3. ice hydrate

Criteria for chemical storage:
a. storage capacity
b. equilibrium pressure
c. operating temperature

1.1 hydride
a. hydrolytic system
   NaBH₄ + NaOH + H₂O → Ru cat. NaBO₂ + H₂ storage capacity 5.3 wt%
   - used in prototype vehicle in a Chrysler Voyager
   - irreversible system
   - not promising in large scale transportation
b. metallic hydride
- hydrogen atoms in the relevant alloys occupy interstices sites in the host lattices.
- typical alloys are \( \text{AB}_5 \) (LaNi, 1.4 wt\%) and \( \text{AB}_2 \) (TiFe, 2 wt\%)
- storage capacities which depend on the occupy interstices sites are low and high price $$$

![Conventional metal hydride](image)

Application: German Navy submarine (Fe/Ti/Mn/Zn Alloy, 1.5 wt\%)

- \( \text{MgH}_2 \):
  - 7.7 wt\%, low cost, good reversibility
  - too stable (equilibrium pressure of 0.1 MPa at 300°C)
  - technologies developed for the destabilization

c. complex hydrides (NaAlH\(_4\))
- hydrogen covalently bound to a metal atom to form a complex anion
- storage capacity depends on the weight of the metals and the number of possible bound hydrogen atoms

decomposition:
- \( 3\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2, 3.7 \text{ wt\%}, 0.1 \text{ MPa at } 30^\circ\text{C} \)
- \( \text{Na}_3\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + 1.5 \text{ H}_2, 1.9 \text{ wt\%}, 0.1 \text{ MPa at } 130^\circ\text{C} \)
- \( 3\text{NaH} \rightarrow 3 \text{ Na} + 1.5 \text{ H}_2, \text{ dec. temp. too high} \)

reforming:
- \( \text{NaH} + \text{Al} \xrightarrow{\text{TiCl}_3/\text{MPa } \text{H}_2 \text{ ball mill}} \text{Ti-doped NaAlH}_4 \)

![Diagram](image)

- d. amine-borane adduct \( (\text{BH}_3\cdot\text{NH}_3) \)

\[
3\text{BH}_3\cdot\text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2 + 6\text{H}_2 \quad \text{19.6 wt\%}
\]
- decomposition steps are exothermic
- irreversible

e. amides/imides

\[
\text{LiNH}_2 + 2\text{LiH} \rightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \rightarrow \text{Li}_3\text{N} + 2\text{H}_2 \quad \text{10.4 wt\%, } 420^\circ\text{C}
\]

1.2. hydrogenation/dehydrogenation of liquid hydrogen carrier
- based on the hydrogenation and dehydrogenation of cyclic hydrocarbons
- benzene/cyclohexane, toluene/methylcyclohexane, naphthalene/decline

![Graph](image)
- *operation temperature is over 300°C*

1.3 ice hydrates
- most well-known system is the methane hydrate present on the floor of the oceans and in the permafrost soil
Mao and coworkers synthesized H₂ hydrate. Science, 2002, 2247
H₂ + H₂O → silt hydrate, (200MPa, < -20°C)

- THF as guest compound stabilize the hydrate, 120 MPa at 0°C
- advantage: non-toxic/non-flammable/non-corrosive materials
- disadvantage: low capacity/need constantly cooled

1.4 Summary
- physical storage is still predominated
  liquid hydrogen for the large volume storage
  high pressure for the small scale storage
- chemical storage is under development
  investigate high storage capacity materials
  thermodynamic and kinetic studies on the current systems

2. Methane Oxidation

CH₄ + H₂O, O₂ → SYNGAS

Hydrocarbons

H₂ + NH₃ → Methanol, DME

HCl, HF

Halocarbons

NH₃

Acetylene

Sulfur

Carbon disulfide

Air → Combustion → Heating → Power generation

Methane is an abundant resource that could serve as an efficient fuel source and chemical feedstock. The known and projected world reserves of natural gas more than 9000 trillion cubic feet are comparable to petroleum. However, the current use of methane is relatively small. Basically, Fisher-Tropsch process is widely used in industry.

2.1 Methane to Methanol

A. Chemical Methods

Methane is a very unreactive molecule, as demonstrated by the high C–H bond strength [D(C-H) = 104 kcal/mol], high ionization potential (12.5 eV), low proton affinity (4.4 eV), and low acidity (pKa = 48). Oxidation of methane encounters problems. Especially, with respect to chemoselectivity, the initial product of oxidation is more reactive toward the oxidant than the methane itself. (In CH₃OH, D(C-H) = 11 kcal/mol). Overoxidation of methanol dramatically reduce the desired product yield.

Transition metal catalyze C-H activation in methane involve:

1. C-H activation by coordination of the methane to the inner sphere of the catalyst (Eⁿ⁺) followed by cleavage of the C-H bond by overall electrophilic substitution to generate Eⁿ⁺-CH₃ intermediate

2. oxidative functionalization involving redox reactions of Eⁿ⁺-CH₃ to generate the desired oxidized product CH₃X.

Catalysts have the features:

1. "soft"-late transition metal
2. highly electrophilic species that form relatively strong covalent bonds to carbon atoms
3. good oxidants

1950, Snyder and Grosse discovered methane oxidation, US patent 2493038

\[
\text{CH}_4 + \text{HgSO}_4 \xrightarrow{\text{cat.}} \text{CH}_3\text{OSO}_3\text{H} \quad 44\%
\]

\[
\text{CH}_4 + \text{H}_2\text{SO}_4, \; 263^\circ C
\]


\[
\text{CH}_4 + \text{PtCl}_6^{2-} + 2\text{H}_2\text{O} \xrightarrow{120^\circ C} \text{CH}_3\text{OH} + 2\text{CH}_3\text{Cl} + 2\text{PtCl}_4^2 + 2\text{HCl}
\]

1: 1

1987, Sen reported Pd(II) catalyzed methane oxidation, JACS, 1987, 109, 819

\[
\text{CH}_4 + 2\text{H}_2\text{O} \xrightarrow{\text{Pd(II)cat.}} \text{CH}_3\text{OCOF}_3 \quad 60\%
\]

"however, there was the reproducibility problem. When Periana tried the same reaction, the yield was less than 5%"

Fig. 1. Methane in industrial processes.
1990, Moiseev discovered Mn(III), Co(III), Cu(II) and Pb(IV) mediated oxidation of methane. JCS, CC, 1990, 1049

\[
\text{CH}_4 + \text{M}^{n+} \xrightarrow{\text{TFA, 180°C}} \text{CH}_3\text{OOCCF}_3
\]

<table>
<thead>
<tr>
<th>Metal salt</th>
<th>Yield, % based on metal oxid. equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(OCCF(_3))(_2)</td>
<td>≤ 0.1</td>
</tr>
<tr>
<td>Mn(OCCF(_3))(_3)</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>Fe(OCCF(_3))(_3)</td>
<td>0</td>
</tr>
<tr>
<td>Co(OCCF(_3))(_3)</td>
<td>90 ± 10</td>
</tr>
<tr>
<td>Cu(OCCF(_3))(_2)</td>
<td>~ 0.1</td>
</tr>
<tr>
<td>Pb(OCCF(_3))(_4)</td>
<td>10 ± 3</td>
</tr>
</tbody>
</table>

In the presence of O\(_2\) the reaction became catalytic (400%) with Co(III) salt. (re-oxidation of Co(II) to Co(III) by oxygen)

1993, Periana and coworker reported Hg(II) catalyzed methane oxidation, Science 1993, 259, 340

\[
\text{CH}_4 + \text{Hg(II) cat.} \xrightarrow{\text{H}_2\text{SO}_4, 180°C} \text{CH}_3\text{OSO}_3\text{H} \quad 43\%
\]

- advantage: product methyl bisulfate greatly reduces the reactivity of the CH\(_3\) group, not only for electrophilic activation but also for radical processes initiated by hydrogen-atom abstraction
- disadvantage: a lot of dilute sulfuric acid generate in reaction system

1997, Sen and coworkers reported a catalytic bimetallic system for methane oxidation. JACS, 1997, 119, 6048

\[
\text{CH}_4 + \text{CuCl}_2, \text{Pd/C, O}_2, \text{CO} \xrightarrow{\text{TFA, H}_2\text{O}, 150°C} \text{CH}_3\text{OOCCF}_3 \quad 300\% \text{ based on Cu}
\]


\[
\text{CH}_4 \xrightarrow{\text{cat. (I)}} \xrightarrow{\text{H}_2\text{SO}_4, 180°C} \text{CH}_3\text{OSO}_3\text{H} \quad 70\%
\]

In this case, N-ligated complexes are better than O-based ligands (high kinetic lability) and P-based ligand (poor oxidative and thermal stability)

2002, Herrmann discovered, ACIEE, 2002, 41, 1745

\[
\text{CH}_4 + \text{K}_2\text{S}_2\text{O}_8 \xrightarrow{\text{cat. } 4c} \xrightarrow{\text{TFA/TFAA, 80°C}} \text{CH}_3\text{OOCCF}_3 + 2\text{KHSO}_4
\]

3000% based on Pd (about 2000% in Periana Pt system)


\[
\text{CH}_4 \xrightarrow{\text{I}_2} \xrightarrow{\text{H}_2\text{SO}_4/\text{SO}_3, 180-220°C} \text{CH}_3\text{OSO}_3\text{H} \quad 45\%
\]

\[
\text{I}_2 + 2 \text{SO}_3 + 0.5 \text{H}_2\text{SO}_4 \xrightarrow{} -0.5 \text{SO}_2
\]

Element sulfur, selenium and tellurium worked well, but at much lower efficiencies.


\[
\text{CH}_4 + \text{H}_2\text{SeO}_4 \xrightarrow{\text{Au}(0)} \xrightarrow{\text{H}_2\text{SO}_4, 180°C} \text{CH}_3\text{OSO}_3\text{H} + \text{H}_2\text{SeO}_3 \quad \text{TON} = 32
\]

45% • \text{H}_2\text{SeO}_4 is known to oxidize gold metal and the same acidic as sulfuric acid
  • Without Se(VI) as additives, Au(III) worked for methane oxidation, however TONs ≪ 1, because Au(0) is not dissolved in hot H\(_2\)SO\(_4\), Au(III) could not be regenerated
2009, Shuth and coworkers, ACIEE ASAP,

Table 1: Catalytic activity of the molecular Periana catalyst and the heterogeneous Pt-CFT and K₂[PtCl₆]-CFT catalysts in methane oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Final methanol conc. [mol L⁻¹]</th>
<th>TON [ₚ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penana catalyst</td>
<td>1.65</td>
<td>158</td>
</tr>
<tr>
<td>Periana catalyst</td>
<td>1.49</td>
<td>355</td>
</tr>
<tr>
<td>K₂[PtCl₆]-CFT</td>
<td>1.54</td>
<td>201</td>
</tr>
<tr>
<td>Pt-CFT</td>
<td>1.80</td>
<td>246</td>
</tr>
</tbody>
</table>

B. Methane biological oxidation - Methane Monoxygenase (MMO)
- the enzymes isolated from methane oxidizing bacteria (Methylococcus capsulatus) contain 4 atoms of non-heme Fe and 1 atom of Cu per molecular weight of 240 000
- schematic active site structure of MMO shows the dimeric iron site involved in dioxygen activation and substrate hydroxylation activity. And redox-active tyrosine residue is also shown
- MMO methane oxidation mechanism is controversial. Here is one well accepted mechanism.

- MMO Mimic system
  Gif chemistry (see GM-alkane hydroxylation)
2.2 Methane to Acetic Acid

\[
\text{cat.} \quad \text{CH}_4 + \text{CO}^{\text{Rh(III)}} \rightarrow \text{CH}_3\text{COOH}
\]

Monsanto process: \( \text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH} \)


\[
\text{CH}_4 + \text{CO}^{\text{Cu(II)} \text{ or Pd(II)}} \rightarrow \text{CH}_3\text{COOH}
\]

best yield was 2960% based on Cu \((\text{Cu(OAc)}_2, \text{K}_2\text{S}_2\text{O}_8)\)

1994, Sen and coworkers reported Rh(III) catalyzed conversion of methane to acetic acid in water. Nature, 1994, 613

\[
\text{CH}_4 \rightarrow \text{RhCl}_3 + \text{H}_2\text{O}, \text{O}_2, \text{CO} \rightarrow \text{CH}_3\text{COOH}
\]

2760% based on Rh(III)

2003, Periana and coworkers reported oxidative condensation of \( \text{CH}_4 \) to \( \text{CH}_3\text{COOH} \). Science, 2003, 814

\[
\text{^{13}CH}_4 + \text{PdSO}_4 \rightarrow \text{^{13}CH}_3\text{COOH}
\]

Evidences for the proposed mechanism:
1. Methanol is not carbonylated under the same condition
2. No ethane were observed
3. No rxn without Pd \((\text{CH}_4/\text{CH}_3\text{OH}/\text{H}_2\text{SO}_4)\)

3. Solar Energy
3.1 Solar Electricity

Solar electricity can be produced from photovoltaic (PV) cells. The commercially available solar cells are currently based on inorganic silicon semiconductors which have reasonable energy conversion efficiencies \((\eta - 15\%)\). However, they require high-purity silicon and skilled manufacturing techniques, which result in high costs, so their widespread use in our lives has been limited. Organic solar cells (dye-sensitized solar cells DSSC), therefore, appear to be a highly promising and cost-effective alternative for PV cells.

How does Dye Sensitized Solar Cell (DSSC) work?
In DSSC, organic dyes are anchored to the surface of semiconducting TiO_2 nanocrystals. The sensitizers absorb the incoming light and are excited. The porous TiO_2 reduce the exited dyes to ground state and give required charge separation. Charges migrate to counter-electrode and electrons go through an external circuit to generate solar electricity.
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Currently, the efforts in synthesis of sensitizers for DSSCs can be grouped into two broad areas:

a) Functional ruthenium(II)-polypyridyl complex

![Black Dye](image)

**Advantages:**
1. wide absorption range
2. high efficiency (11%)

**Disadvantages:**
1. expensive Ru $$$
2. tricky synthesis and purifications

b) Metal free organic donor-acceptor dyes

- replace Ru(II) complex
- widen the scope of available sensitizers
- extend the electronic properties of materials

![Donor and Acceptor](image)

Requirements in the molecular design of organic dyes for DSSCs:
1. the organic dye must have at least one anchoring group (-COOH, SO₂H, -PO₃H₂, -OH) for adsorption onto the TiO₂ surface
2. To achieve efficient electron injection from the excited dye to the conduction band of TiO₂, the energy level of LUMO of the dye must be high (more negative) while HOMO must be low (more positive)
3. have high absorption over the wide region of sunlight (high light-harvesting efficiency)
4. chemical stability in the photo reaction cycle (durable DSSC)
5. avoid dye aggregation (π-stacked aggregation of D-A-π conjugated dye)
6. suppress recombination of injected electrons (efficient charge separation)

Some typical organic dyes for DSSCs:

- **Coumarin dyes, η = 8.2 %**
- **Indoline dyes, η = 9.5 %**
- **Squaraine dyes, η = 4.5 %**
  "Near-Infrared Dye"
- **Perylene dyes, η = 6.8 %**
- **Cyanine dyes, η = 9.5 %**
3.2 Solar fuel - direct production of fuel from sunlight

A. Natural photosynthesis

converts sunlight into fuel, producing biomass and over geological time, fossil fuel (500,000 times slower than consuming)

Ethanol fuel from the biomass:

- Plant (corn, sugar cane): \(6\text{CO}_2 + 6\text{H}_2\text{O} + \text{Light} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2\)
- Fermentation: \(\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{CO}_2 + \text{Heat}\)
- Engine: \(\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + \text{Heat}\)
- Net: \(\text{Light} \rightarrow \text{Heat}\)

Currently, only sugar (surgar cane) and starch (corn) can be economically converted into ethanol. Cellulosic ethanol is hot research area where the cellulose part of plant is broken down to sugars and subsequently converted to ethanol.

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"Can chemistry help in solving the energy problem?"

"YES! Chemistry can play a key role in improving any kind of energy-related technology and can even find novel solutions. Finding a breakthrough for solving the energy crisis is indeed the "grand challenge" of chemistry."