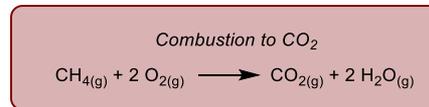
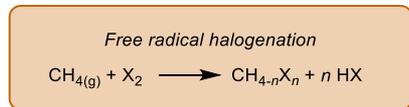
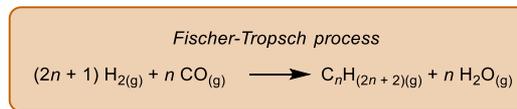
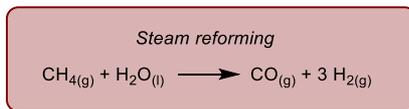


## Methane in Chemical Industry

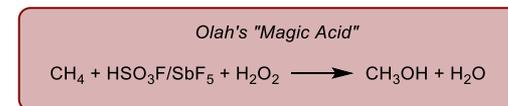
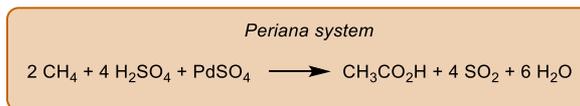
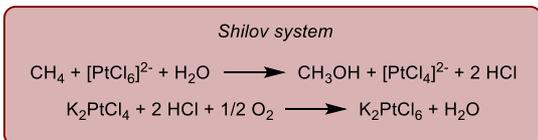
- Produces most of the world's hydrogen gas
- Energy intensive ( $\Delta H = 206$  kJ/mol)
- Produces all our favorite solvents and ozone depleting substances



- Produces liquid hydrocarbons for use as fuel or carbon sources
- Most of the methane gas obtained from petroleum drilling is burnt unproductively

## Selective Methane Oxidation

- Generally difficult – oxidation products often easier to oxidize than methane, producing CO<sub>2</sub>
- Holy grail: Efficient, cheap, green functionalization of methane
- Many academic advances, none practical on industrial scale



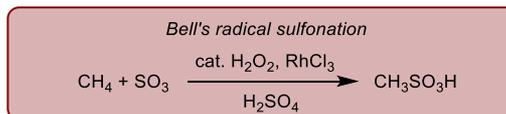
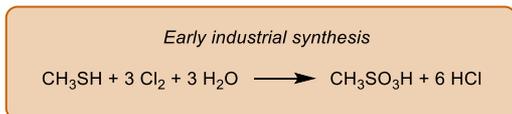
- Low turnover frequency & turnover number
- Mixture of products obtained
- Pt(IV) stoichiometric oxidant

- Low turnover number, palladium black forms
- Mixture of products obtained

- Esoteric and expensive reagent used

Periana, R. A. *Chem. Rev.* **2017**, *117*, 8521. <https://doi.org/10.1021/acs.chemrev.6b00739>

## Sulfonation of Methane

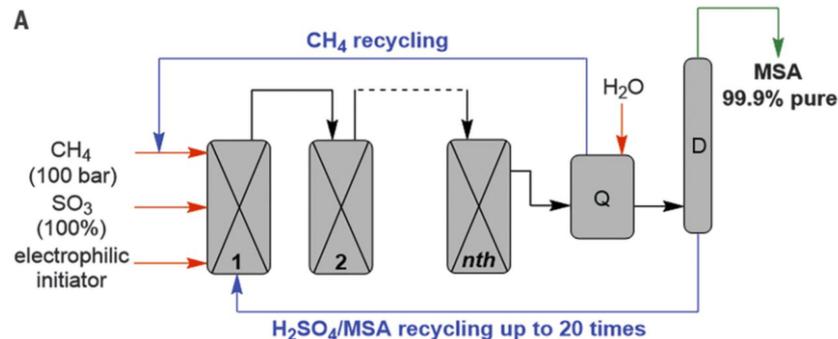
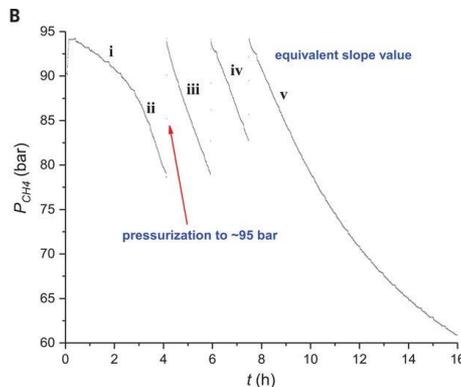
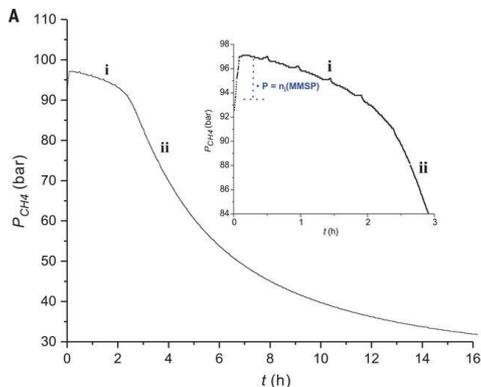
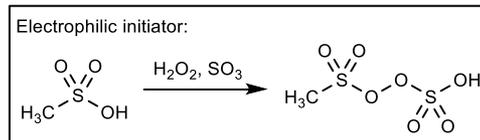
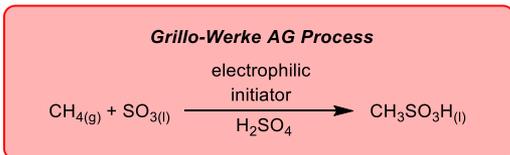


### Uses for methanesulfonic acid:

- Strong organic acid
- Use in electroplating industry
- Industrially relevant reagent
- Used as a rust remover

Bell, A. T. *Angew. Chem. Int. Ed.* **2003**, *42*, 2990. <https://doi.org/10.1002/anie.200350976>

## Reaction and Optimization



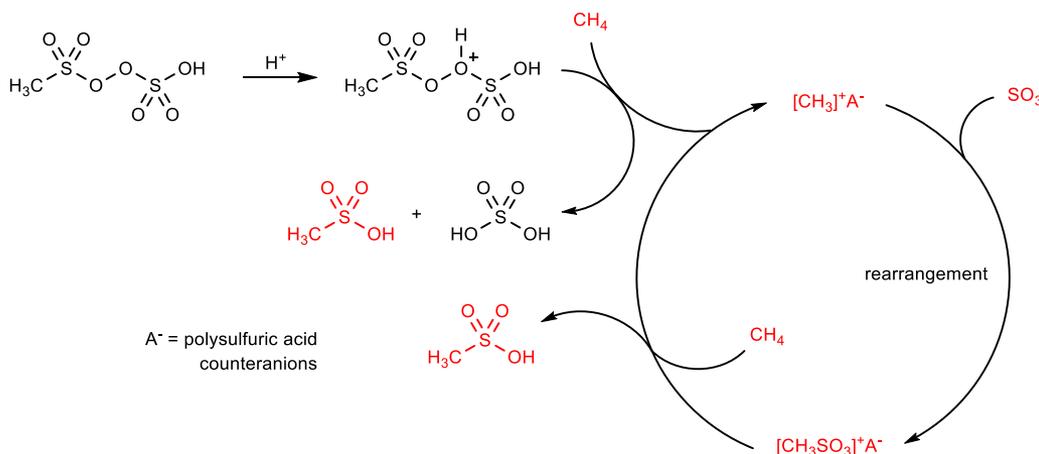
### Pilot plant facility able to produce:

- 200 kg pure MSA in 2 weeks
- 2.3 tons MSA in 80 days
- **20 tons MSA per year**

At 50 °C, reaction **99.9% selective for MSA**

At 85 °C, mixture of MSA, SO<sub>2</sub>, methyl bisulfate produced

## Proposed Catalytic Cycle and Rationale



### Evidence for cationic chain reaction:

- < 1% deuterium incorporation using SO<sub>3</sub>/D<sub>2</sub>SO<sub>4</sub>
- No ethane or higher order sulfonyl alkanes detected
- Adding O<sub>2</sub> as a deactivating agent did not affect rate as drastically as previous radical sulfonations
- Activating sulfonyl peroxide with UV irradiation did not lead to productive catalysis

### A Controversial Mechanism

- Many chemists challenged the originally proposed CH<sub>3</sub><sup>+</sup> species, leading to the paper's revision