
ETH zürich

Group activity Industrial Chemistry
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Acetic Acid

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1 Preparation

1.1 Oxidate acetaldehyde

1.2 Methanol carbonylation



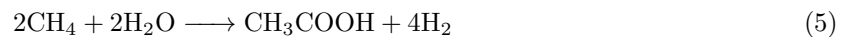
Only Syngas as feedstock:



Or from natural gas (CH_4)

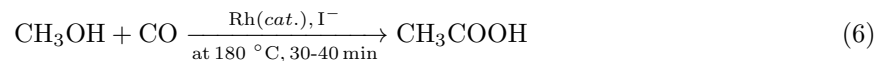


(3) and (4)



1.3 Monsanto's acetic acid process

Homogeneous catalytic carbonylation of methanol using a $\text{Rh}^{\text{I}}/\text{Rh}^{\text{III}}$ catalyst.



Why Iodide? CH_3I is always the substance for carboxylation Good nucleophile, weak base, good leaving group

Conditions: 30-60 atm, 150-200°C

Selectivity: up to more than 99%

Drawbacks:

- Rh also catalyses the water gas shift reaction => undesired side products
- Propionic acid as a side product: The system produces acetaldehyde which is reduced by H_2
- Instability of the cat. in CO-deficient areas => inactive species is formed, cat. is lost

1.3.1 Mechanism

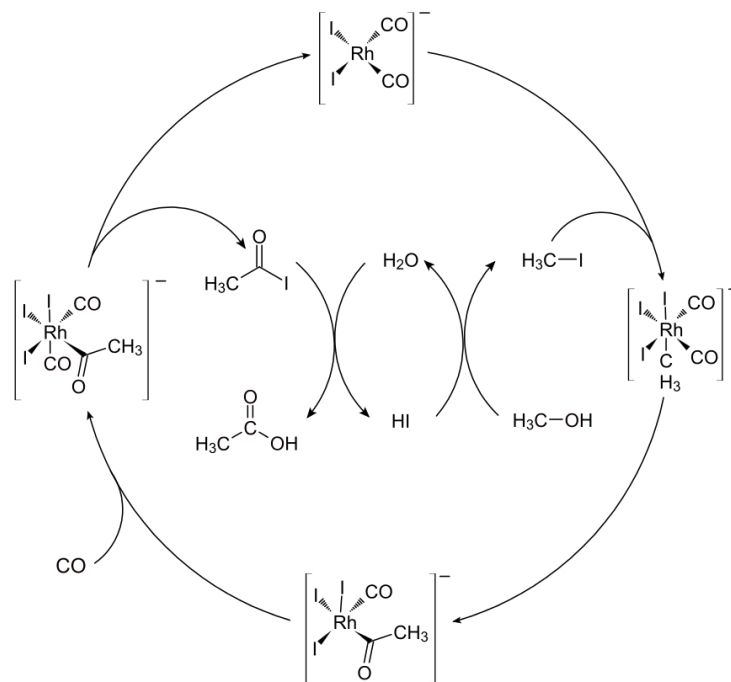


Abbildung 1: Catalytic Cycle of the Monsanto's acetic acid process

1.4 Cativa process

- has higher activity and selectivity
- higher cat. stability and activity
- Chemicals: Ir catalyst, I^- and a lewis acid (promotor)
- allows water content
- needs less water content than Monsanto process
 - decreases water-gas shift reaction
 - increases selectivity for acetic acid
 - decreases the effort needed for drying
- Mechanism is more complicated, due to neutral intermediates
- rds is changed from the oxidative addition to the migratory insertion of CO
 - involves elimination of iodide
 - rds is promoted with species that form iodide complexes
- more environmental-friendly
- Ir is 29% cheaper than Rh (99.9% pure metal by mole)

Catalyst: a $\text{Ir}^{\text{I}}/\text{Ir}^{\text{III}}$ catalyst. Promoters: W, Re, Os or ZnI_2 , CdI_2 , HgI_2 , CaI_2 , InI_3 , $[\text{Ru}_2(\text{CO})_c]_n$

Promoters must accept an iodo ligand.

1.4.1 Mechanism

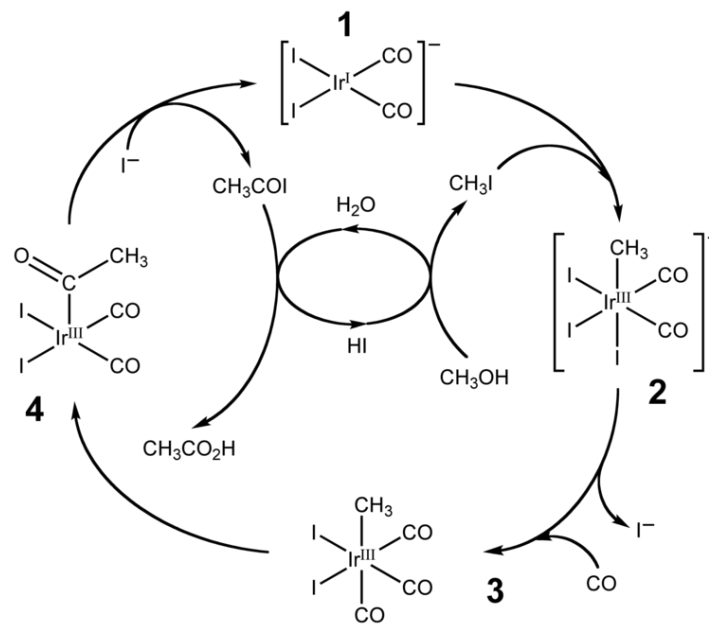


Abbildung 2: Catalytic Cycle of the cativa acetic acid process

1.5 Use of Acetic Acid

- polymers PVA (Polyvinyl Acetate)
- artificial silk
- solvents
- additives (textiles, dye, medicine)
- synthetic intermediates (e.g. acetic anhydride)

2 Methanol Production

From synthesis gas:



Both reactions are exothermic. The used catalysts are Cu-ZnO-Al₂O₃ catalysts.

2.1 Plant

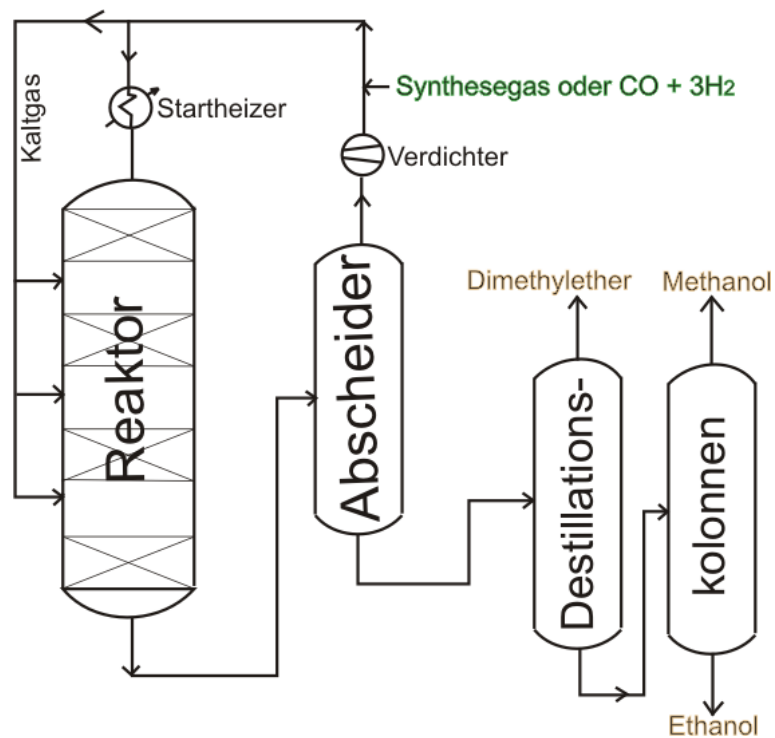


Abbildung 3: Plant for methanol production

2.2 Use of Methanol

- Solvent
- Reagent in the Cativa Process => Acetic acid
- Energy carrier
- Fuels

3 Ammonia Production



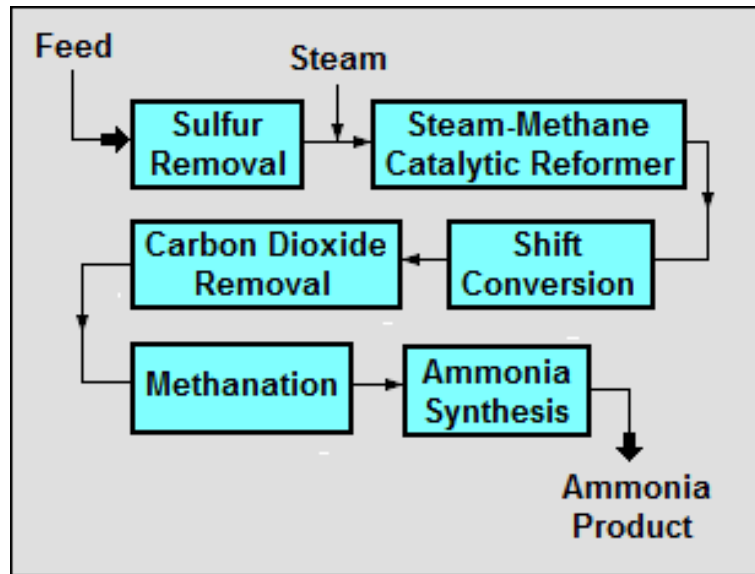


Abbildung 4: Production of ammonia

3.1 Use of Ammonia

main byproducts is CO₂ (can be used for Methanol production)

4 Questions

Question 1: How do we produce acetic acid?

Use of biomass/bio-fuels:

- Fermentation/oxidation of EtOH (result: 5% acetic acid in water)
- Destructive distillation of ...
- Wet oxidation of cellulose
- Anaerobic fermentation

=> from all this we do not get pure acetic acid: diluted, AcOH, separation issues

From fossil fuels

- Methanol carbonylation
- Butane oxidation
- Acetaldehyde oxidation

Comment on the oxidative fermentation of Ethanol: $\text{EtOH} + \text{O}_2 \longrightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$

- Acetobacter Bacteria is used
- up to 20% AcOH results

Question 2: What are the main uses of acetic acid?

Chemical uses: Polymer synthesis (PVA), solvent production, artificial silk, synthetic intermediates, ester production, acetic anhydride (> 1/4 of acetic acid used for this)

=> feedstock: fossil fuels; biomass can be used if the purity does not matter

Food and Medical Uses: Vinegar (fermentation of biomass), perfumes (scent depends on biomass feedstock), antiseptic 100% purity, screening process for cervical cancer (18th century)

=> feedstock: biomass (simplifies the approval of a certain standard which has to be fulfilled in this industry)

Comment on the environmental impact: biomass in general is more environmental friendly **but** we get diluted products -> we need energy to separate the product from the solvent/side product = high environmental impact

Question 3: Analyze the feedstock of acetic acid from raw materials.

Acetic aldehyde as a precursor

- Wacker process: Oxidation of ethylene, Pd catalyzed
 - Steamcracking of ethane
 - => Byproduct H_2 : Ammonia Synthesis, CH_4
 - Steamcracking of naphtha

Methanol as a precursor

- $2 \text{MeOH} + \text{CO} \longrightarrow 2 \text{CH}_3\text{COOH}$
- MeOH is produced from natural gas:
 $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3 \text{H}_2$
 $\text{CO} + 2 \text{H}_2 \longrightarrow \text{MeOH}$
- Syngas could be produced from coal gasification **but** we only produce 1 eq H_2 (would need two)
=> the excess hydrogen can be used for our ammonia production (therefore we choose this option and do not perform steam reforming with 2 eq. C)

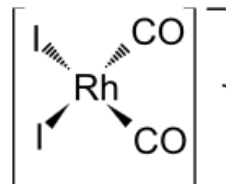
Question 4: How to insert the CO into the MeOH?

Monsanto Process: via migratory insertion

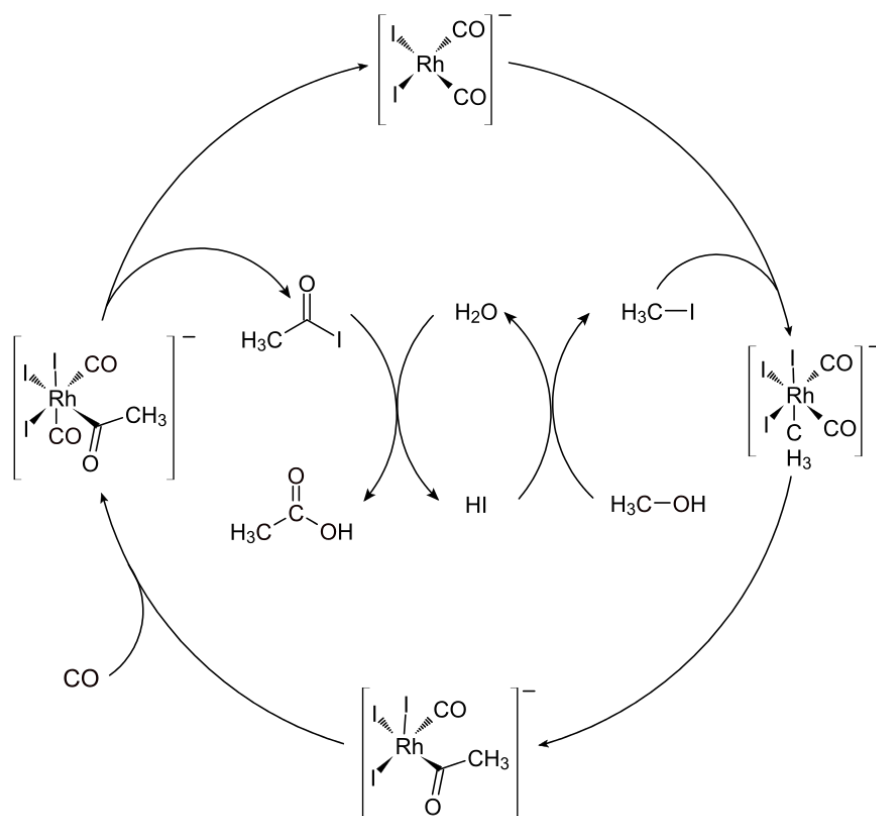
- if we only add MeOH we would bind at the oxygen but no carbon
=> activation with iodide which produces MeI
- MeI reacts with the complex, where the carbon is bound to the metal

Question 5: What is the structure of the used Rh complex?

Square planar, negatively charged



Question 6: Complete the catalytic cycle



Question 7: The oxidative step is rate limiting. How can you increase the rate?

- Have more MeI in the system (a higher concentration)
but: for the production of MeI we also produce HI which is corrosive
=> we could solve this with using a water free process, where HI is not corrosive
- Increase the concentration of the cat.

Another solution would be the use of Ir instead of Rh: increasing electron density -> rds is changed from the oxidative addition to the migratory insertion

Question 8: What is the consequence of increasing concentration of HI? How can we deal with it in the reactor design stage?

Increasing the HI concentration in this process means more corrosive acidic species. Two options to prevent this during the design phase would be to

- use corrosion resistant materials for our reactor(s)

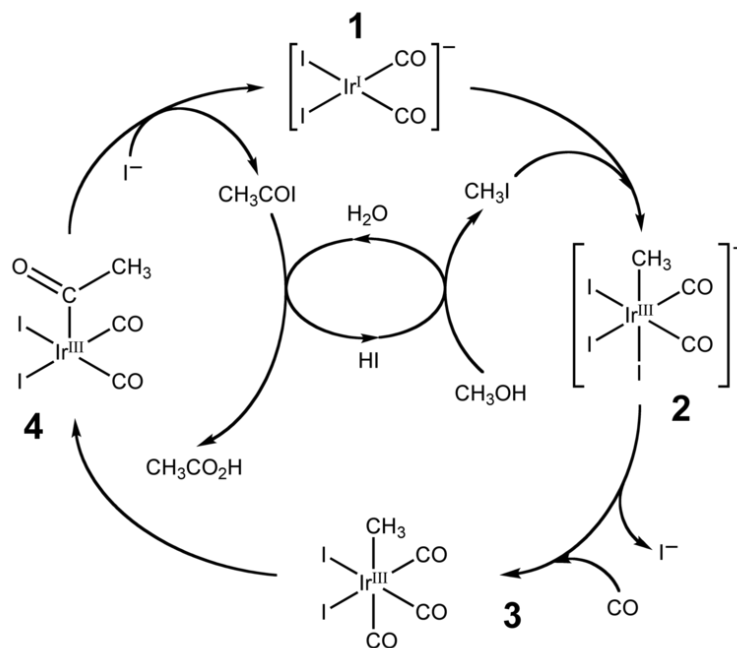
or

- use a reaction pathway without H₂O to remove the HI's capability to form an acid.

Question 9: Our head of system and process analysis told us that designing a reactor that can withstand the conditions required for the Rh catalyst are too expensive. We also need to use too many separation units due to the high water concentration. What can we do?

We can use an Ir catalyst instead of the Rh catalyst (i.e. the Cativa process). This process needs less water and has a higher yield, therefore resulting in less corrosive reaction conditions and needing fewer separation units.

Question 10: Complete the catalytic cycle



Question 11: The migratory insertion now becomes rate limiting. What can we do about it?

- We can use a promoter which binds Iodide (a complex) to accelerate the separation of Iodide

Question 12: How does the promoter enter in the catalytic cycle?

- $[\text{RuI}_2(\text{CO})_3]$ and ZnI_2 are able to abstract/scavenge Iodine from Structure 2 and HI respectively, thereby increasing the carbonylation rate.
- After being scavenged the Iodine can not act as a poison to the migratory insertion = crucial criteria

A detailed description of the described effects can be found in literature [1].

Additional Question: Reactor Design of the Cativa Process

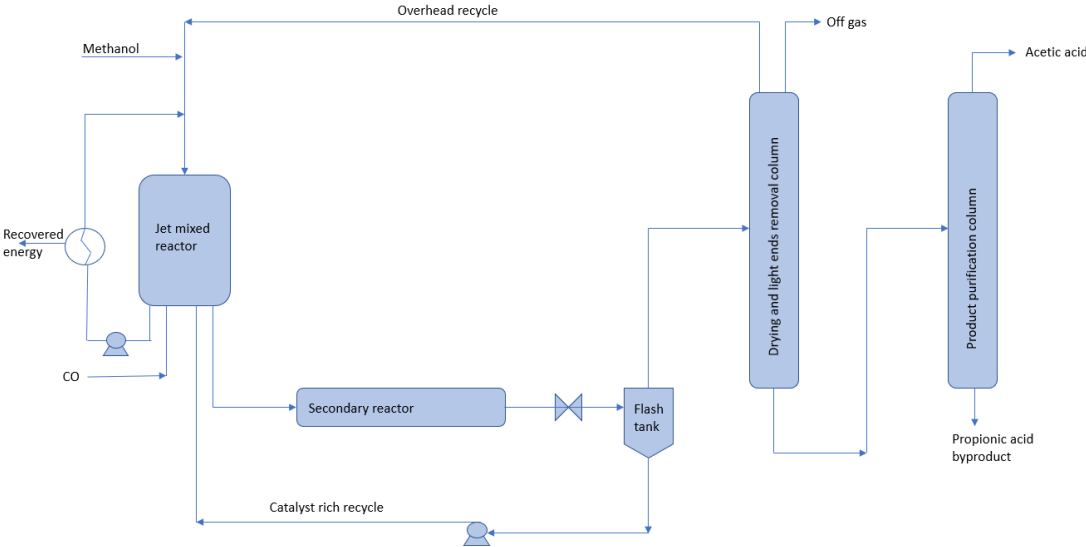


Abbildung 5: The proposed reactor design for the Cativa-Process.

5 Notes

Question 1: Use of biomass/ bio-fuels

- fermentation/oxidation of ethanol (only 5% acetic acid in water)
- destructive distillation of
- wet oxidation of cellulose
- anaerobic fermentation

=> you do not get pure acetic acid (mix of various solvents): diluted, AcOH, separation issues

- Methanol carbonylation
- Butane oxidation
- Acetaldehyde oxidation (Wacker oxidation of ethylene is bound to this)

Oxidative fermentation:

- Acetobacter Bacteria
- up to 20% AcOH
- $\text{EtOH} + \text{O}_2 \longrightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$
- CSTR with O_2 bubbling through
- 15% batch in 24h, 20% batch in 60hrs

Main uses of acetic acid?: What feedstock is used + chemical uses

- Polymer synthesis (PVA)
- Feedstock can be any chemical that was discussed before (for other uses it sometimes has to be considered for reasons of purity)
- Solvent production
- Artificial silk (cheaper than normal silk)
- Synthetic intermediates
- Ester Production
- Acetic anhydride (more than 1/4 used for this)

=> there are lot of chemicals which come from acetic acid (this list includes the most important ones)

=> feedstock: fossil fuels, if purity does not matter too much also biomass can be used

food and medical uses:

- Vinegar (Biomass through fermentation)
- Perfumes (Scents change with different Biomass feedstocks)
- Antiseptic 100% purity
- Screening process for cervical cancer (18th century)

=> generally from biomass feedstocks (simplifies approval of a certain standard which has to be fulfilled in this industry)

comment: from biomass we get diluted products -> we need energy to separate it from the side products
fossil fuels give pure products -> less energy to separate => environmental impact has to be seen in a broad view

Acetic acid from raw materials? Acetic acid as a precursor

- Wacker process: Oxidation of ethylene, Pd catalyzed

-
- Steamcracking of ethane
 - Byproducts: H₂ -> Ammonia synthesis, CH₄
 - steamcracking of naphtha
 - $2\text{C}_2\text{H}_4\text{O} + \text{O}_2 \longrightarrow 2\text{CH}_3\text{COOH}$
 - hydroformylation is not an option as one carbon is added
 - methanol production with reactions 3 and 4 in our file
 - instead of reaction 3: syngas can be produced from coal $\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$
=> we only have 1 equivalent of H₂ here which is why we use methane
=> additionally hydrogen can be used for ammonia production
 - we could twice steam reform coal but as we also have an ammonia production we choose the steam reforming of methane to have excess hydrogen

How to insert CO in MeOH?

- Use cat with iodide
- otherwise the CO is inserted between the CH bond
- two processes: Monsanto or Cativa, both have HI as their side product
- Monsanto: side products CO₂, H₂
- via migratory insertion of the CO in the metal complex

Discussion:

- add Me and CO to the complex -> migratory insertion
- if we only add MeOH we would bind at the oxygen but not carbon
=> activation with iodide -> MeI -> reaction with complex
- MeI + Metal -> addition of -I and -Me (Monsanto process)

What is the structure of the cat?

- square planar, negative charge
- 2 I- ligands, 2 CO- ligands, Rh(I) metal

How can we accelerate the rds (oxidative addition)?

- have more MeI in the system/higher concentration (but HI is corrosive and used for the production)
- have a higher concentration of the cat
- if the reaction is water free we don't have corrosion problems as then we have an acid base reaction
=> but here we clearly have water

=> amount of water increases (as more MeI production = more water)

- we could use Ir instead of Rh -> increasing electron density
- rds is changed from the oxidative addition to the migratory insertion

Literatur

- [1] Anthony Haynes u. a. “Promotion of Iridium-Catalyzed Methanol Carbonylation: Mechanistic Studies of the Cativa Process”. In: *Journal of the American Chemical Society* 126.9 (2004). PMID: 14995202, S. 2847–2861. DOI: 10.1021/ja039464y. eprint: <https://doi.org/10.1021/ja039464y>. URL: <https://doi.org/10.1021/ja039464y>.